THE STRUCTURE OF MOLECULES

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THE STRUCTURE OF MOLECULES

Edited by

P. DEBYE

Professor of Experimental Physics and Director of the Physical Institute at the University of Leipzig

Authorized Translation by

WINIFRED M. DEANS, M.A., B.Sc.

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PREFACE TO THE GERMAN EDITION

For the fourth time it was found possible, thanks to support from the Ministry of Education of Saxony, to hold a small and intimate conference in Leipzig on a specialized subject. Owing to the kindness of the lecturers and the enterprise of the publishing firm of S. Hirzel, the proceedings of the conference have again been made available to a wider public in book form.

The papers on this occasion dealt with problems of molecular structure. The general purpose and hence the contents of this book will be best summarized by a brief account of the programme which determined the choice of the papers.

The first problem confronting the worker in this subject is that of the geometrical structure of the molecule, i.e. of the arrangement of the atoms in space. This is at once the oldest and the most central problem of chemistry, which was solved in a very striking way on the basis of purely chemical experiments by setting up definite structural formulæ. In recent years, however, new methods have been added to the purely chemical ones; these new methods are extending previous knowledge, prove of great service in connexion with certain points where no definite conclusions can be drawn from chemical reactions alone, and supplement the structural formulæ with absolute data for the distances between the atoms in the molecule. In the paper by K. L. Wolf, these modern methods are tested on the problem of free rotation about the carbon-carbon bond. Molecules, it is found, are by no means rigid forms: even at ordinary temperatures the distances between the atoms frequently deviate very considerably from their mean values. Very valuable data on these oscillations have been supplied by band spectroscopy. Accordingly the second paper, by R. Mecke, though partly devoted to rotations of the molecule as a whole, deals chiefly with these molecular vibrations, with the express purpose of working up the experimental data in order to make general statements about the

"elastic strength" of atomic bindings. As is well known, our knowledge of atomic vibrations has been extended in an important way by observations on the Raman effect. In the third paper, therefore, the atomic motions are considered from this point of view by F. Rasetti. Unexpected complications are exhibited e.g. by the CO_2 molecule and are explained by Fermi as due to internal resonance phenomena. Thanks to remarkable developments in technique it is also possible to observe Raman effects in crystals fairly conveniently and hence to reach new conclusions about the atomic motions in solid bodies.

In Rasetti's paper the question which vibrations occur chiefly in the infra-red spectrum and which in the Raman effect plays an important part. G. Placzek then brings forward a comprehensive theory of the relationship between the intensities of the scattered lines and the symmetry of the molecular structure. He also explains the polarization of the scattered lines and specially emphasizes the importance of quantitative observations of this effect.

In all these papers the motions of the atoms in the molecule are only taken account of in so far as they do not endanger the existence of the molecule as such. These motions, however, may become so marked that the molecule breaks up into its constituent parts. How this may arise on irradiation, what interesting peculiarities may thereby appear, what final products (atoms or ions) arise from the dissociation—these are the subjects of Miss H. Sponer's paper. Very closely related to dissociation phenomena is the phenomenon which V. Henri calls predissociation and which is manifested by the occurrence of blurred bands. R. de L. Kronig reports on the interpretation of these phenomena as non-radiating transitions to continuous energy-levels and the conditions for their occurrence. A general survey of the experimental material by V. Henri himself completes the picture in a very appropriate way.

In none of the above papers has the cause of atomic binding been discussed. The special energy relationships which alone make a stable molecule possible depend on special electronic structures. It thus comes about that the whole matter is only rounded off by G. Herzberg in the last paper, where valency problems and their connexion with electronic structure are brought into the foreground.

Many of those able to attend the conference felt that it gave them not only a comprehensive survey of the whole subject but at the same time a wide prospect of future developments along various lines. It is hoped that this stimulating effect will be extended to a

wider circle of investigators by publication of the lectures in book form.

I should like to take this opportunity of again thanking Dr. H. Sack for his very valuable assistance both in organizing the conference and in seeing this book through the press.

P. DEBYE.

LEIPZIG, *September*, 1931.

PUBLISHERS' NOTE

The present book is a translation of *Molekülstruktur* (Leipziger Vorträge, 1931), published by S. Hirzel, Leipzig. For the English edition some emendations and additional references have been supplied by the authors.

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THE STRUCTURE OF MOLECULES

Problems of Free Rotation about Single and Double Carbon Bonds

K. L. WOLF,* KIEL

In order to explain certain empirically-derived rules about the number of possible isomers of organic compounds, the idea has been put forward by organic chemists that parts of molecules which are connected by a C=C bond are not free to rotate about the bond, whereas the possibility of "free rotation" about the line of the single C—C bond is assumed. The statement about the double bond is perfectly definite and admits of only one possibility; the chemical data, on the other hand, admit three possible types of "free rotation" about the C—C axis. Hitherto these have not been discriminated by chemical methods, and it may be that such a discrimination can only be made with great difficulty. The three cases are as follows:

1. The two halves of the molecule rotate about the connecting line indifferently or almost indifferently.
2. Equilibrium is rapidly attained between various configurations with differing azimuths.
3. For some reason or other (meanwhile assumed unknown) practically only one definite configuration exists at any one time.

In attempting to discover the physical meaning of the two postulates of stereochemistry mentioned above, therefore, the main thing is to restate the principle of free rotation more accurately on the basis of physical measurements, while in the case of the double

* Written in collaboration with W. Bodenheimer and W. Herold; the paper was read by W. Herold.

bond we have merely to give the theoretical interpretation of a definite empirical result.

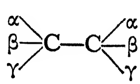
This refinement of the idea of " free rotation " is now possible on the basis of a number of physical data. Owing to lack of space we cannot go into details here, and accordingly content ourselves with the following brief summary of the conclusions which we have been led to draw from dipole moment experiments, interference experiments in gases and vapours, anisotropy of polarization, and the variations of optical activity and of the dipole moment with temperature.

If a molecule contains several polar groups so arranged that according to the structural formula they are " free to rotate " about a C—C bond relative to one another, it is clear that in general (the distance between the polar groups being prescribed) the *third* conception stated above holds good for *low* temperatures, the *second* for *medium* temperatures, and the *first* for *high* temperatures.

Thus absolute rigidity and complete freedom of rotation occur as limiting cases for low and high temperatures respectively.* Here it may be advisable to measure the temperatures according to a reduced system, the necessary data for its establishment being supplied by the magnitudes of the energy maxima and minima.

Further, we see from purely electrostatic considerations that (the absolute temperature being assumed constant) the nearer the polar groups whose effects on one another prevent free rotation are to one another, the longer is the time during which the limiting case of low temperature may be regarded as realized. This is the meaning which must be given to the results stated in column 6 of Table I, where the one case of independence of temperature (COOH) is to be ascribed to the parts of the molecules still remaining rigidly connected together in the minimum potential position, and the other (*p*-di-R-oxybenzene) to complete freedom of rotation.

As is easily seen, we accordingly have to reckon with the existence of several potential minima † in molecules with neighbouring groups which are free to rotate relative to one another. In molecules of the type



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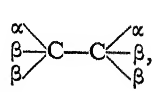


* K. L. Wolf, *Trans. Faraday Soc.*, **26**, 315, 351 (1930).

† Discussed on the basis of data on the specific heat of ethane by L. Ebert *The Dipole Moment and Chemical Structure*, p. 70 (Blackie & Son, Ltd., 1931).

TABLE I

Dipole Moments of Substances with Groups which are " Free to Rotate "

Substance: Name	Substance: Formula	Groups	Distance between Groups	Dipole Moment: Magnitude	Dipole Moment: Temperature Effect
Carboxyl group . .	—COOH	CO OH	1·5 Å.	Small (corresponds to anti-parallel position).*	Independent† of temperature at room temperature.
Dichloro-ethane . .	Cl—CH_2—CH_2Cl	Cl Cl	3 Å.	Smaller than the value calculated for free rotation.	Increases‡ by 10% between $-70°$ and $+30°$.
Quinol di-ether . .	RO——OR	OR OR	6 Å.	Corresponding to the value calculated for free rotation.‖	Independent of temperature.‡

* K. L. Wolf, *Zeitschr. f. phys. Chemie*, B, 3, 128 (1929).

† This is shown e.g. by measurements, which have not yet been published, on the effects of temperature on the dipole moments of aliphatic esters.

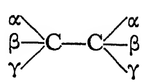
‡ L. Meyer, *Zeitschr. f. phys. Chemie*, B, 8, 27 (1930).

‖ K. L. Wolf, loc. cit. The values $1{\cdot}23 \,.\, 10^{-18}$ for the moment of anisole (Donle and Volkert, *Zeitschr f phys. Chemie*, B, 8, 60 (1930)) and $1{\cdot}28 \,.\, 10^{-18}$ for the moment of phenetole (K. Petri, *Dissertation*, Kiel (1931)) are to be regarded as correct.

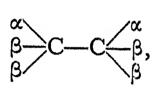
for example, there are three potential minima, which in general will differ in depth, so that in molecules of this type the configuration with most pairs of identical groups in the *trans*-position will be the stable one, or the most stable one. This involves the existence of several isomers which may be transformed into each other and which co-exist in thermal equilibrium, but which may not be known to the chemist because they cannot be readily isolated. (These isomers we shall call *rotational isomers* because they are merely distinguished by the differing relative azimuths of the halves of the molecules and are otherwise of identical structure.) We would hence be led to conclude (although the fact has not yet been proved) that in molecules of this type the relationship between temperature and molecular polarization will vary according as the substance is brought to the various temperatures slowly or rapidly (" freezing " of the equilibrium corresponding to the higher temperature).

A further statement, to which we have just been able to give precision here in Leipzig as a result of interferometric experiments, is that in molecules where the stable *trans*-position exists practically alone, the halves of the molecule execute oscillations about the position of stable equilibrium, and that the values found for the magnitude of these oscillations are reasonably consistent with the measured values of the dipole moment (when this differs from zero).* It is not yet known, however, how these oscillations are quantized. Information on this point should be obtained from absorption experiments in the remote infra-red, and at low temperatures possibly also in the region of very short electric waves.†

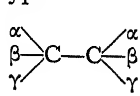
On the whole the results derived from the above-mentioned physical data are quite definite, at least for simpler molecules of the type



or



so that it is worth while to attempt an attack on this basis on chemical problems where progress is meanwhile at a standstill. For such purposes molecules of the type



* Personal communication from Professor Debye.

† For the same reason, special attention should be paid in investigations of the Raman effect to scattered lines of slight displacement.

are particularly suitable, as in this case it is possible to isolate isomers which are structurally distinguished merely by the arrangement of the substituents in space. The characteristic features distinguishing these isomers are briefly summarized below; the importance of this in what follows cannot be over-emphasized.

The occurrence of two asymmetric carbon atoms means that the different isomers will exhibit different amounts of rotation of the plane of polarized light. It is found, in fact, that two of the known isomers, which apart from rotatory dispersion are identical in all their physical and chemical properties,* are distinguished solely by the sign of their rotations, which are numerically equal, while the third isomer, which exhibits no rotation, differs from them in its properties (melting-point, boiling-point, heat of combustion, &c.). According to our ideas of optical activity, the occurrence of these isomers is to be taken as meaning that in the *meso*-form, which exhibits no rotation and cannot be decomposed into optical antipodes, the substituents are arranged about the carbon atoms in such a way that whenever two identical substituents (say a, a_1) approach one another as closely as possible as a result of rotation of the halves of the molecule (take up the *cis*-position), the two other pairs of substituents also take up the *cis*-position; similarly, as we see by rotating the halves of the molecules through 180° from the *cis*-position, all the identical substituents can in the *meso*-form simultaneously occupy the *trans*-position relative to one another. On the other hand, the two optical antipodes, which differ from one another merely as an object and its mirror image do, are so constructed that all three pairs of groups cannot simultaneously take up the *cis*-position or the *trans*-position relative to one another, but if one pair of substituents is in the *cis*-position the others occupy a position very near the *trans*-position.

Now according to the preceding we should be able to discriminate between rotational isomers which have not yet been isolated by chemistry, both in the active forms and in the *meso*-form.†

* These isomers and their racemic mixture which does not rotate the plane of polarization will be referred to as "active forms", as here we are not concerned with the differences between them. The above considerations in fact apply only to the free molecules individually (to vapours, dilute solutions, &c., but not to pure liquids or solid bodies), which apart from the rotatory dispersion exhibit no difference in physical and chemical properties in the three possible active forms.

† As regards the possibility of detecting the separate rotational isomers, see K. L. Wolf and W. Bodenheimer, *Zeitschr. f. phys. Chemie*, Bodenstein volume, p. 620 (1931).

From observations of the dipole moments and the effects of temperature on the optical activity, it is found that in the tartaric acid derivatives there actually exist three rotational isomers in thermal equilibrium among themselves, i.e. that the halves of the molecule do not rotate freely relative to one another but show a preference for the positions of minimum potential energy, as was stated above. The above-mentioned differences in chemical and physical behaviour are then at once explained by the differing depths of the energy minima in the active and *meso*-forms due to the differing arrangement of the substituents about the carbon atoms. Here we may expect (and this is confirmed by experiment) that with increasing temperature these differences will decrease in such a way that above a temperature which permits free rotation the differences will vanish entirely.

If in particular we consider the dipole moments * of the *meso*-form and the active form, these must be distinguished by the magnitude of their total moment, which is obtained by vector addition of the binding moments, which are equal in pairs. As the absolute *trans*-position corresponds to the smallest potential energy and also to the smallest dipole moment, we further deduce that the moment of the *meso*-form should always be smaller than that of the active form, since in the latter case, as we have said before, it is out of the question for all the pairs of substituents to occupy the exact *trans*-position relative to one another at once. If all the individual moments lie in the directions of the C—α and other bonds, the absolute *trans*-position of the *meso*-form gives a zero moment, and a deviation from this value can only be explained by oscillation about the equilibrium position of least kinetic energy, that is to say, by the simultaneous existence of a certain percentage of the metastable rotational isomers.

The results of moment experiments on substances of the type $(C\alpha\beta\gamma)_2$ are summarized in Table II as far as they are available. In stilbene dichloride, in which there are no bent substituents, the moment of the *meso*-form amounts to only 40 per cent of the moment of the active form, and even this small value must be ascribed to the oscillations mentioned above, i.e. to the occurrence of metastable rotational isomers.

In all the other substances adduced the resultant moments of

* For the first discussion of this group of related questions by means of dipole moment experiments see K. L. Wolf, *Trans. Farad. Soc.*, **26**, 315, 351 (1930); W. Bodenheimer, Diploma thesis, Karlsruhe (1930).

one or more substituents are inclined to the C—X bond, so that a priori we should expect to obtain a finite value for the resultant moment even in the case of the *meso*-form. Our statement that the moment of the *meso*-form should be the smaller, however, is everywhere fulfilled even here, except in the case of the diethyl ester of tartaric acid, in which a particularly strong "intramolecular solvation" of the OH groups obviously plays a part.

TABLE II

Dipole Moments of Molecules of the Type $H-\underset{R_2}{\overset{R_1}{C}}-\underset{R_2}{\overset{R_1}{C}}-H$

R_1	R_2	$\mu \cdot 10^{18}$ active form	$\mu \cdot 10^{18}$ *meso*-form	Observer*
$-OH$	$-COOC_2H_5$	3·10	3·66	B
$-OH$	$-COOCH_3$	2·93	†	B
$-OCH_3$	$-COOC_2H_5$	3·74	3·34	B
$-OCH_3$	$-COOCH_3$	3·16	2·79	B
$-Cl$	$-COOCH_3$	3·00	2·40	B, H and N
$-OH$	$-C_6H_5$	2·67	2·05	W and S
$-Cl$	$-C_6H_5$	2·75	1·25	W and S

As we know from the behaviour of monovalent and polyvalent alcohols, the OH groups have a pronounced associating or solvating effect; this is also the explanation of the peculiar behaviour of dihydroxysuccinic (tartaric) acid. A similar peculiarity is exhibited by the moments of the esters of tartaric acid and by many properties of the acid itself, e.g. the melting-point. The *meso*-form of tartaric acid, in fact, melts at a lower temperature than the active form, whereas in the other substituted succinic acids the melting-point of the *meso*-form is the higher, as has been recently shown in attempts to resolve the racemic mixture of these acids into optical antipodes. In Beilstein's *Handbuch der organischen Chemie* the acids have been classified in such a way that in analogy with tartaric acid

* Observers: Bodenheimer, Diploma thesis, Karlsruhe (1930), and *Dissertation*, Kiel (1931–2) (on the variation with concentration in benzene at 22° C.); Hassel and Naeshagen, *Zeitschr. f. Electrochemie*, **36**, 736 (1930); Weissberger and Sängewald, *Zeitschr. f. phys. Chemie*, B, **9**, 133 (1930); **12**, 399 (1931).

† The dimethyl ester of *meso*-tartaric acid could not be investigated owing to its insolubility in non-polar solvents.

the form with the higher melting-point is called the active form (in Beilstein, "fumaroid") and the form with the lower melting-point the *meso*-form ("malenoid"), so that the classification given there is wrong for those substituted succinic acids for which no proof of constitution is given. This erroneous nomenclature has been adopted * in papers by Kuhn † and Hückel.‡

The result of the dipole moment experiments, that in the *meso*-form the *trans*-position is the preferred one, should be capable of verification by interferometric measurements of the intramolecular distances. As, however, the theoretical interpretation of interferometric measurements is very difficult and perhaps impossible at present in the case of such complicated substances containing so many mobile groups and with substituents differing so little in atomic number, the absorption of the above-mentioned substances in dilute heptane or ether solution was measured in order that further distinctions might be drawn between the active form and the *meso*-form. From absorption experiments with other substances in solvents with various dielectric constants we know that the position and shape of the absorption curves depend to a great extent on the strength of the fields of force of the molecules of the medium, or, in chemical language, on the strength of solvation.§ As for the substances in question the effect of extramolecular solvation will be particularly trifling with heptane as solvent and the intramolecular solvation is different for the active and *meso*-forms, we must expect to find a difference in the position and appearance of the absorption curves of the COOH group in the esters and of the benzene ring in stilbene dichloride, the differences in the absorption curves being related to the differences in the dipole moments.

Fig. 1 shows that in the cases where the *meso*-form (*b*) has the smaller moment (dichlorosuccinic ester and dimethoxysuccinic ester, curves IV and III), the absorption curve of the COOH group lies in a region of greater wave-length than the curve for the active form (*a*), whereas the absorption curve of the diethyl ester of

* The resolution has been accomplished in the case of dimethylsuccinic acid and diethylsuccinic acid: see Table V, p. 19.

† Kuhn, *Ber. d. dtsch. chem. Ges.*, 58, 2091 (1925).

‡ Hückel, *Zeitschr. f. angew. Chemie*, 39, 848 (1926).

§ See e.g. G. Scheibe, *Ber. d. dtsch. chem. Ges.*, 58, 586 (1925); K. L. Wolf, *Zeitschr. f. phys. Chemie*, B, 2, 39 (1929); K. L. Wolf and W. Herold, *Zeitschr. f. phys. Chemie*, B, 12, 165 (1931).

meso-tartaric acid (I) lies on the side of smaller wave-length relative to the active form. That is, in all three cases the larger moment is associated with absorption in the region of shorter wave-length, and, as may be verified at the same time, it is also associated with the less well-defined structure. If we consider the absorption bands of the two dimethyl esters of tartaric acid (II), where the moment of the *meso*-form could not be measured owing to the insolubility of the substance in non-polar solvents, we observe that the position of the curves is the same but the definiteness of structure differs

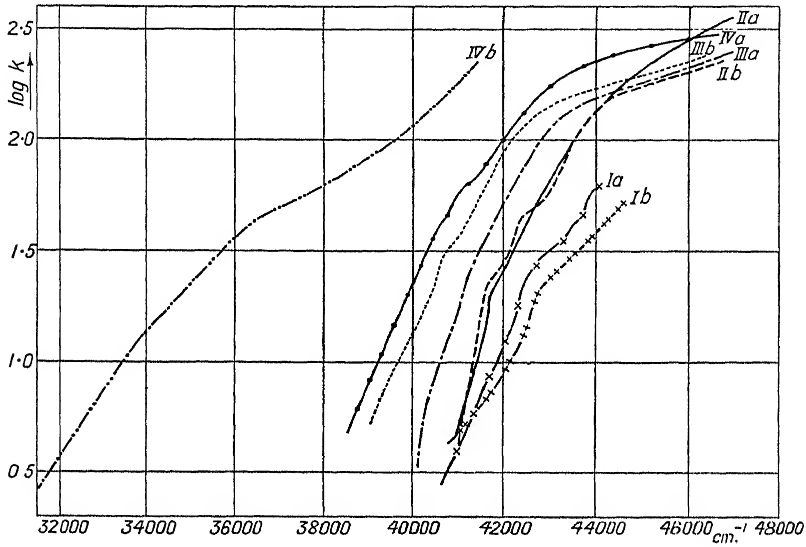


Fig. 1

in the two cases, the *meso*-form being the better defined. If we bear in mind what we have said above it follows that according to the position of the bands the moments are almost equal, whereas according to the definiteness of structure the moment of the *meso*-form should be the greater; the latter is the result obtained by direct measurement with the diethyl ester.

In order to discuss the nature of " internal solvation " in more detail, it is necessary to study the effect of "extramolecular solvation" experimentally and draw conclusions as to which groups in the active and *meso*-forms have the stronger effect in " intramolecular solvation " on the position and shape of the absorption bands. An example of measurements of this kind, which are meanwhile

being carried out for a number of substances, is given in fig. 2, where, in addition to the results of experiments in heptane solution (IV*a*, *b*,), the results of experiments in methyl alcohol solution (IV*a*′, *b*′) are shown. We see that the "extramolecular solvation" by the dipole fields of the OH groups of the alcohol gives rise to a displacement of the absorption region of the COOH group towards the violet, just as is known to occur with the absorption region of the CO group in aldehydes and ketones. At the same time the definiteness of the structure is enhanced in the dimethyl ester of

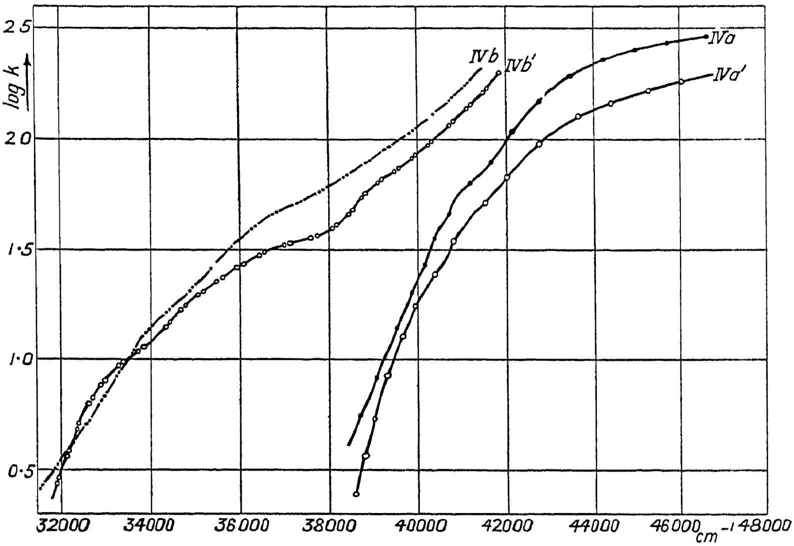


Fig. 2

meso-dichlorosuccinic acid; this, however, may be a special property of this substance, as judging from the absorption in heptane solution it obviously takes up a special position; this is possibly brought about by the strong effect of the two chlorine atoms on the carboxyl group.*

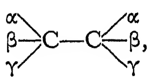
With reference to the absorption curves of the two stilbene dichlorides, if we take account of the fact that the absorbing benzene residue of *meso*-stilbene dichloride in the *trans*-position is exposed to a stronger effect of the two chlorine atoms than in the active form, and assume certain facts established in a paper meanwhile

* In the *trans*-position of the *meso*-form the second chlorine atom is very near the carboxyl group.

in the press * on the demonstration of additive and alternating properties of benzene derivatives, we deduce that in this case the absorption curve of the *meso*-form (provided the conclusion drawn from the moment experiments, i.e. that the *trans*-position is the preferred one, is correct) should exhibit a greater displacement of position and a greater heightening of the curve as compared with the absorption curve of benzyl chloride than that of the active form. The results of experiment † confirm this conclusion ($\log k_{max} = 2{\cdot}4$ for benzyl chloride, i.e. 2·7 for 2 benzyl chloride molecules; 2·77 for active stilbene dichloride, 2·88 for *meso*-stilbene dichloride, i.e. the heightening amounts to 18 per cent for the active form, 50 per cent for the *meso*-form).

The results of the above-mentioned physical investigations on the substances of type $(C\alpha\beta\gamma)_2$ considered may in general be summarized as follows.

In the possible rotations of the two halves of the molecule relative to one another there exist special positions of minimum potential energy. The most stable configuration is that in which all identical groups occupy the *trans*-position relative to one another; this, however, is possible in the *meso*-form only. At low temperatures there is no free rotation, but the molecule by preference takes up positions of minimum potential energy such that at moderately low temperatures (quantized) oscillations may take place about the most stable equilibrium position, i.e. an equilibrium is set up between various rotational isomers. The oscillations and the equilibrium between rotational isomers must alike depend on the temperature, by a theorem of Boltzmann. It follows that for the temperature variation of the moment of a molecule of the form



in which all the group moments lie in the directions of the C—α, C—β, and C—γ bonds, we can theoretically calculate how the potential varies as one half of the molecule rotates about the other, if we know the individual moments and the distances apart of the individual substituents. The value of the dipole moment, in fact,

* K. L. Wolf and W. Herold, *Zeitschr. f. phys. Chemie*, B, **13**, 201 (1931), and experiments as yet unpublished on triply-substituted benzene, undertaken with O. Strasser as a continuation of the above work.

† From experiments by H. L. Donle, published in the paper by K. L. Wolf and W. Bodenheimer, *Zeitschr. f. phys. Chemie*, Bodenstein volume, 620 (1931).

will at first increase as the temperature rises (in the *meso*-form from the value zero, in the active form from a finite value), until the temperature is reached for which the mean kinetic energy is just sufficient for rotation to occur. This rotation, however, is by no means uniform or unhindered, for the mean interval of time during which the positions of maximum potential are occupied is greater than that spent in the positions of minimum potential (for the reasons which cause a pendulum to linger in its extreme positions). A very pronounced preference for the positions of maximum potential, however, implies a maximum value of the dipole moment. Hence when, owing to further rise of temperature,

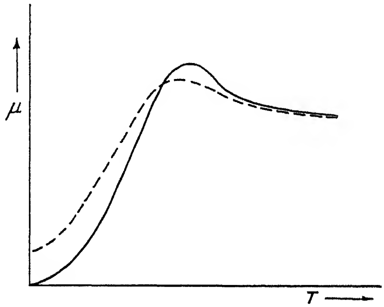
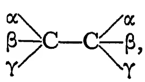


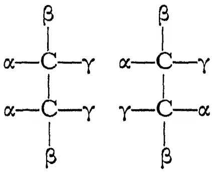
Fig 3

the molecule can more readily pass the positions of maximum potential, i.e. when the molecule approaches uniformity of rotation, the resulting moment must diminish a little and asymptotically approach a limiting value. As the *meso*-form has the lowest minimum of potential in the *trans*-position, and the highest maximum in the *cis*-position, the maximum of the dipole moment is most well-marked in this form. The effect of temperature on the dipole moments of the two forms is therefore somewhat as shown in fig. 3. The whole course of the T, μ curve is meanwhile being investigated experimentally in our laboratories for 2 : 3-dichlorobutane and 2 : 3-dibromobutane (by interferometric measurements of the intramolecular distances and measurements of the dipole moments in dilute solution and if necessary in the gaseous state).

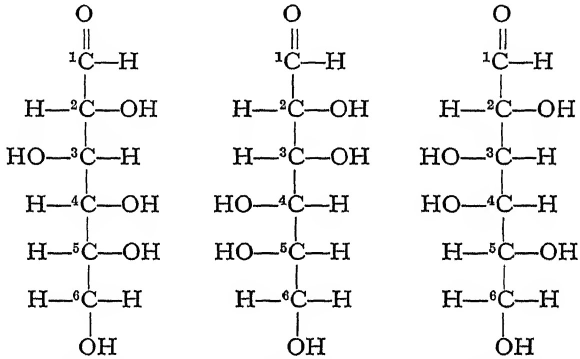
We shall now use these results relating to the geometrical arrangement of the atoms or groups of atoms in compounds of the type



in order to explain certain chemical phenomena which have not been satisfactorily interpreted hitherto. First, however, we shall show by recent optical experiments that even in such complicated compounds as the carbohydrates, simple electrostatic considerations like those above are capable of throwing some light on the mechanism of reaction. The case we shall discuss is that of the aldehyde-pyranose equilibrium of the three aldohexoses glucose, mannose, and galactose. From the chemical structural formulæ of these hexoses it follows, in analogy with the configurations of the *meso*- and active forms of the compounds $(C\alpha\beta\gamma)_2$, that the three pairs of substituents H, OH, and hydro-carbon residue in glucose attached



meso-form   active form

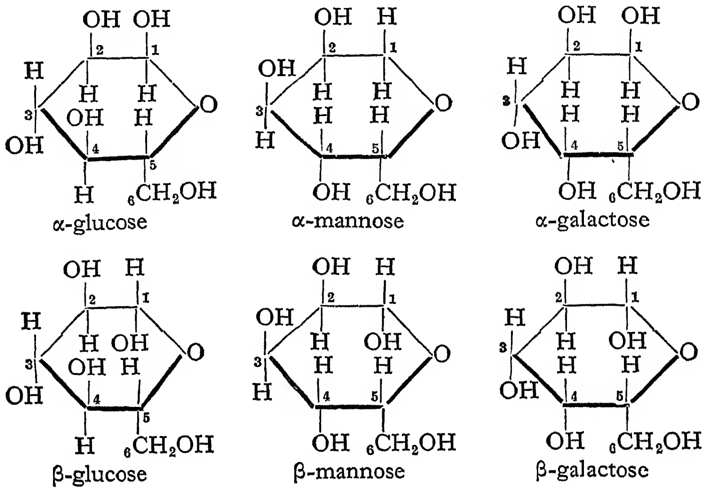


glucose   mannose   galactose

Aldohexoses

to the asymmetric carbon atoms 2, 3 and 3, 4 can never all be simultaneously in the *cis*-position, while if one pair of substituents attached to the carbon atoms 4, 5 is in the *cis*-position, the others must also occupy the *cis*-position. The same is true for mannose and galactose. If we now form the pyranose forms of these aldoses (shown on p. 14), it follows that in β-glucose the H and OH groups can only occupy the *trans*-position, seeing that the hydrocarbon residues must occupy the *cis*-position; in α-glucose the groups attached to the carbon atoms 2, 3 and 3, 4 occupy the *trans*-position and only those attached to the carbon atoms 1, 2 occupy the *cis*-position. According to what we have said above the configuration in which all or as many as possible of the pairs of substituents occupy the *trans*-position is the most stable; that is, the pyranose form should be more stable for glucose than for mannose and galactose, as in α-glucose only one pair and in β-glucose no pair of H and OH

groups occupies the *cis*-position, whereas in the other two aldoses one pair of groups occupies the *cis*-position in the β-form and two



pairs in the α-form. The tendency towards rupture of the pyranose ring with re-formation of the free aldehyde form should therefore be less in glucose than in mannose and galactose.

Now by means of absorption experiments * we have measured † the percentage of intact CO groups, i.e. of the free aldehyde form, present in aqueous solutions of these three sugars in varying concentration, and found that glucose contains about 0·1 per cent of the free aldehyde form, whereas mannose contains about fourteen times as much and galactose about fifty times as much. As the aldehyde-hydrated aldehyde equilibrium cannot differ very much in the different aldoses, the differing behaviour of the three sugars must be ascribed to the differing stability of the pyranose forms. The result of the optical measurements, therefore, is entirely in agreement with the previous discussion.

We now return to the consideration of the substituted succinic acids. The most striking feature of their behaviour, which cannot be satisfactorily explained from the chemical side, is the fact that the active and *meso*-forms of the acids and anhydrides can be transformed into one another with or without catalysts, definite con-

* W. Herold and K. L. Wolf, *Zeitschr. f. phys. Chemie*, B, **12**, 165 (1931).

† Preliminary results, which are being tested more accurately; cf. also Niederhoff, *Zeitschr. f. phys. Chemie*, **165**, 130 (1927); **174**, 300 (1928).

figurations being preferred. On the basis of our physical investigation of the structure of these substances this behaviour may be explained as follows. The most stable form is that in which *all* identical groups, or if that for any reason is impossible, as many pairs of polar groups as possible, occupy the *trans*-position. Then the most stable form of the free acids is the *meso*-form, as in this all the identical groups can simultaneously occupy the *trans*-position, and, as we have seen, do in fact take up this position at low temperatures. In the anhydride, on the other hand, one pair of groups, namely the carboxyl groups, must take up the *cis*-position; in the *meso*-form the other groups would also occupy the *cis*-position, whereas in the active form they would take up approximately the *trans*-position. The active form is accordingly the more stable form of the anhydride. We may expect from this that removal of water from the active acid will give practically only the active anhydride, whereas, although the *meso*-acid probably gives rise primarily to the *meso*-anhydride, the high temperature necessary for the removal of water causes partial transformation into the more stable active form. If the *acid* is the final product (resulting e.g. from the anhydride taking up water), the *meso*-anhydride will probably give rise to the *meso*-acid only and the active form will primarily give rise to the active acid; transformation of the latter into the more stable *meso*-acid is possible but scarcely probable if the hydration or transformation of the acid is carried out at low temperature (cf. Table III).

TABLE III

Rules for Transformation of Dicarboxylic Acids of Type

$$\begin{array}{ccccc} & & R_1 & & R_1' \\ & & | & & | \\ HOOC & - & C & - & C - COOH \\ & & | & & | \\ & & H & & H \end{array}$$

and their Anhydrides

Compound	Product of Reaction	Stable Form of Product of Reaction	Compound likely to occur
Acid	Anhydride	Active	
Meso			Active + meso
Active			Active
Anhydride	Acid	Meso	
Meso			Meso
Active			(Meso) + active

Table IV, which contains substituted succinic acids for which data relating to transformation are available, shows that in cases 1–5, in which the active form has been identified chemically by resolution of the racemic mixture into optical antipodes, our postulate is fulfilled, i.e. the final products of reaction are predominantly the *meso*-acid and predominantly or exclusively the active anhydride. In cases 6–9 it has not been established by chemical means which is the active form, and which the *meso*. If we now find that in transformation of the two forms A and B the acid consists predominantly of the form A and the anhydride predominantly or exclusively of the form B, we may, in view of the obviously definite validity of the rules given in Table III, regard form A as the *meso*-form and form B as the active form, as is done with the substances 6–8 and 10–15 in Table IV.* Di-isopropylsuccinic acid alone fails to be definitely classified by this scheme. The form B certainly predominates when the anhydride is formed, but a considerable quantity of form B is also produced along with form A in the transformation of the acid, so that B cannot be identified with the active form with absolute certainty.†

In the last few substances (10–15) in Table IV the substituents R_1 and R_1' are different, so that even the form in which H, the carboxyl group, and the residue simultaneously take up the *cis*-position is capable of being resolved into optical antipodes. Meanwhile, therefore, a proof of constitution by resolution into optical antipodes is out of the question, and a really definite proof of constitution by substitution can only be carried out with great difficulty, owing to the readiness with which Walden inversion takes place. On the basis of the rules given in Table III, however, we can definitely settle in which form simultaneous *cis*-positions are possible, at least so long as the two substituents R_1 and R_1' do not have opposite charges or do not differ markedly in polarity. By analogy with the term *meso*-form, we call the form in which the pairs of groups can simultaneously occupy the *cis*-position the *mesoid form*,‡ and reserve the term *active form* for the other form.

As regards the mechanism of transformation the following statements may be made. By far the greater number of organic

* The resolution of diethylsuccinic acid has meanwhile been carried out by Bodenheimer and the results confirm our classification.

† It is quite possible that owing to the large space occupied by the isopropyl groups complications due to steric hindrance arise.

‡ Indicated by × in Table IV.

TABLE IV

Results of Transformation of Dicarboxylic Acids of the form

$$\begin{array}{ccccc} & R_1 & & R_1' & \\ & | & & | & \\ HOOC— & C & — & C & —COOH \\ & | & & | & \\ & H & & H & \end{array}$$

	R_1	R_1'	Final Product: Acid (with Melting-point)	Final Product: Anhydride	Proof of Constitution
1	CH_3	CH_3	active $\rightleftharpoons$ meso 135° (129) 209°	meso → active	resolution *
2	C_6H_5	C_6H_5	active → meso 220° (183) 229°	meso → active	,, †
3	Cl	Cl	active → meso 174° 217°	meso → active	,, ‡
4	Br	Br	active → meso 166° (151) 261°	meso → active	,, §
5	OH	OH	active $\rightleftharpoons$ meso 170° (210) 140°	meso → active	
6	C_2H_5	C_2H_5	active → meso 119° 208°	meso → active	(resolution ‖)
7	C_3H_7	C_3H_7	active → meso 119° 182°	meso → active	
8	*iso*-C_4H_9	*iso*-C_4H_9	active | meso 97° 193°–195°	meso → active	
9	*iso*-C_3H_7	*iso*-C_3H_7	A →? B 171° 226°–228°	A → B	
10	CH_3	C_2H_5	active → meso× 101° 235°–237°	meso× $\rightleftharpoons$ active	
11	CH_3	C_3H_7	active | meso× 92° 156°	meso× → active	
12	CH_3	*iso*-C_3H_7	active → meso× 125° 171°	meso× $\rightleftharpoons$ active	
13	CH_3	$CH_2C_6H_5$	active → meso× 138° | 159°	meso× $\rightleftharpoons$ active	
14	CH_3	C_6H_5	active → meso× 130° 192°	meso× → active	

* Werner Basyrin, *Ber. d. dtsch. Chem. Ges.*, **46**, 3230 (1913).

† Wren and Still, *Journ. Chem. Soc.*, **107**, 444 (1913).

‡ Holmberg, *Chem. Zentralblatt* (1912), II, 1618.

§ Holmberg, *Chem. Zentralblatt* (1911), II, 1432.

‖ See footnote (*) on p. 16.

reactions either proceed rapidly in the absence of catalysts at high temperatures only, and do not occur or proceed only very slowly at low temperatures, i.e. the heat required for activation is large; or, on the other hand, the heat of reaction is so great that it is essential to use dilute solutions or make special arrangements for cooling. Reactions which proceed mildly, i.e. those which without catalysts or irradiation proceed with considerable velocity without developing a great deal of heat even when the concentrations are great, are probably very rare. To form an idea of the energies involved we recall that many transformations may be induced by irradiation with ultra-violet light of wave-length about 3000 Å. A molecule thus irradiated possesses after absorption of one quantum a store of energy corresponding to a temperature of several thousand degrees. If organic molecules are subjected for long to a temperature of this magnitude their structure is completely annihilated. Organic reactions, however, generally take place in the liquid state or in the gaseous state under very high pressure, and under these conditions a molecule which happens to be hotter than its surroundings rapidly loses its high temperature by collision with other molecules. During the brief interval when the molecule has a high temperature, however, the intramolecular bonds are loosened without the separate atoms or groups having time to leave the region of the molecule; that is, the idea of fixed valencies in definite directions loses all meaning and a regrouping of the substituents may occur. This is probably all that can be said at the present time about the mechanism of transformation.

The simpler of the di-substituted succinic acids which we have just been discussing are usually represented by adding on the substituents to the double bond of fumaric acid or maleic acid and their homologues. If both substituents are the same, the ideas developed above lead us to form the following idea of what happens, e.g. when Cl_2 is added on. The chlorine molecule approaches sufficiently close to a molecule of the unsaturated acid for us to speak of the formation of an association complex. Now no matter what position the chlorine molecule takes up relative to the molecule of the acid, it is always more probable from energy considerations that in the formation of the saturated compound the two similarly charged chlorine atoms will attempt to take up positions in the molecule as far distant from one another as possible. In fumaric acid, in which two pairs of groups already stand practically in the *trans*-position, the *trans*-position then in general results, and *meso*-

acid is formed. In maleic acid the two pairs of groups stand practically in the *cis*-position, and the attempts of the introduced substituents to take up positions as far apart as possible lead to the formation of active acid; the same is true for maleic anhydride. Table V, in which the relevant data are summarized, shows that in the addition of identical substituents like Cl_2, Br_2, H_2 (and even

TABLE V

Formation of Substituted Succinic Acids by addition of substituents at the double-linked carbon atoms

Formula	Substituent	Acid		*Cis*-anhydride
		trans	*cis*	
COOH . CH : CH . COOH	Cl_2 Br_2 HOCl	**Meso** **Meso** Meso	**Meso** Meso Meso (active)	**Active** **Active**
$\mathrm{COOH\,.\,CH : \overset{\overset{\displaystyle CH_3}{\vert}}{C}—COOH}$	Cl_2 Br_2	**Meso** **Meso**	Meso Meso	
$\mathrm{COOH\,.\,\overset{\overset{\displaystyle CH_3}{\vert}}{C} = \overset{\overset{\displaystyle CH_3}{\vert}}{C}\,.\,COOH}$	H_2	Meso		

in the reaction with HOCl, which falls apart into the equally charged substituents OH and Cl) the *trans*-acid gives rise almost quantitatively to *meso*-acid, the *cis*-acid to a mixture of active acid and *meso*-acid, and the *cis*-anhydride exclusively to active anhydride. On our assumptions about the mechanism of the addition of substituents, this means that the *meso*-acid formed from the *trans*-acid continues to exist, being the most stable form; the same is true of the active anhydride formed from the *cis*-anhydride. On the other hand, the active acid which is probably primarily formed from the *cis*-acid would partly be transformed into the more stable *meso*-form owing to the heat evolved in the reaction.

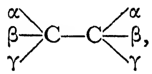
If in contradiction to any considerations which are plausible from the energy point of view we assume for a moment that the two atoms introduced take up a position as near to one another as possible (i.e. the *cis*-position) in spite of their similar charges, the

trans-acid would give rise to the active form, which according to experimental results must largely be transformed into the more stable *meso*-form; the *cis*-anhydride would give the *meso*-anhydride, which according to experiment would be transformed almost quantitatively into the more stable active form. In view of what we have said above, however, this is scarcely consistent, and the most probable mechanism of reaction is still the addition of substituents in the *trans*-position, as discussed above. A question that cannot be definitely settled is whether in *trans*-addition to the *cis*-acid (maleic acid) the active form is primarily formed and is then partially transformed into the more stable *meso*-acid, or whether the *cis*-acid (maleic acid) is primarily transformed partially into the more stable *trans*-acid (fumaric acid), the *cis*-form then giving rise to the active acid in the addition reaction and the *trans*-form to the *meso*-acid. For it has been proved that maleic acid is partially transformed into fumaric acid under the action of bromine. This transformation of maleic acid into fumaric acid by foreign substances may be explained either by intermediate formation of a saturated compound, i.e. destruction of the double bond, or by catalysis pure and simple. If we apply E. Hückel's quantum ideas to the C—C double bond, it is quite conceivable that under the influence of catalysts the two halves of the molecule may rotate once about the plane of the π-electrons, which would cause an exchange of *cis* and *trans*.

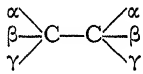
Another problem of free rotation should perhaps be treated in a similar way. In the case of a number of simple unsaturated compounds it has not hitherto been found possible to represent two isomers as *cis*-form and *trans*-form. If in these substances the substituents attached to the doubly-linked carbon atoms are so constituted that one carbon atom receives a strong positive induced charge and the other a strong negative induced charge, it is conceivable that, in view of the known ready and anisotropic polarizability of the double bond, the normal distribution of the negative charge is so markedly disturbed that a rotation or at least a single change-over of the two halves of the molecule is possible in spite of the double bond. Then in any subsequent reaction in which the *cis-trans* isomers are produced or separated either the more stable form would always arise owing to intramolecular transformation, or no marked difference between the *cis*-form and the *trans*-form would exist. The chemical data should be surveyed from this point of view; of course it cannot be stated definitely

whether this application of Hückel's theory is justifiable, as our knowledge of the double bond is still too slight.

Summary.—From consideration of certain properties of substituted succinic acids and the diastereoisomeric aldehexoses it appears that the relationships governing rotation about the single carbon bond, and also the structure of the asymmetric carbon atom, which were discussed in the first half of the paper, enable us to give a simple explanation of certain phenomena in organic chemistry which hitherto have not been satisfactorily accounted for. Considerations resembling those brought forward here may readily be applied to a much wider range of material, in particular to the transformation phenomena in compounds of the type



such as occur in the series of reactions dicarboxylic acid $\rightleftharpoons$ amic acid $\rightleftharpoons$ imide.* In conclusion we may point out that considerations similar to those applied here to the transformations and modes of formation of compounds of the type



should also enable us to explain other transformations, in particular the phenomena occurring in the Walden inversion (the differing behaviour of alkalis and moist silver oxide). Here again we must always start from the fundamental principle that the controlling feature in substitution is not the presence of directed valencies, but the dynamical process of addition of the substituent to the reacting molecule.

* Von Auwers, *Ann. d. Chem.*, 387, 16 (1912); for further details see W. Bodenheimer, *Dissertation*, Kiel (1931–2).

Experimental Results obtained from Band Spectroscopy of Polyatomic Molecules

R. MECKE, HEIDELBERG

My account of the experimental results of band spectroscopy of polyatomic molecules must not be regarded as a report on a branch of study which has already led to definite conclusions. In the case of the spectra of polyatomic molecules—in contradistinction to those of diatomic molecules—we are still only in the initial stages of investigations which may not yield results of any note for several years. Thus I am unfortunately compelled to begin my report with negative statements, pointing out the numerous difficulties with which the investigator of band spectroscopy is faced when the number of atoms in the molecule rises from two to three or more. In this way, however, we shall become acquainted with the paths along which the spectroscopic investigation of polyatomic molecules is likely to advance in the immediate future. I also hope to be able to show how even now many statements may be made about the structure of polyatomic molecules if we employ a composite method of investigation, namely, use infra-red measurements (both thermal and photographic) in conjunction with data obtained from Raman spectra and the quantitative methods of molecular interferometry. In discussing these positive results, however, I must confine myself to a more limited section of the subject, and I shall accordingly conclude by giving a special account of a problem which in the present state of investigations I consider particularly important, namely the *calculation and explanation of the proper frequencies of a polyatomic molecule*. My reason for considering the solution of this problem so important is that I believe that the colossal amount of data on Raman spectra, which has swollen like an avalanche during the last few years, can only thus be fruitfully applied not only to physical problems relating to the molecule but also to chemical problems.

I. As is well known, the spectrum of a diatomic molecule (electronic vibration spectrum) is analysed by obtaining the moment of inertia of the molecule, i.e. the internuclear distance, from the "fine structure" of the bands by means of the so-called "combination principle", the "gross structure" of the system of bands being then fitted in a similar way into a band-head diagram which immediately gives us the frequency of the nuclear vibration and the degree of anharmonic binding. Further, attempts are being made to determine the character of the electron terms from the type of structure of the bands, and finally to ascertain the products of molecular decomposition which are formed when the nuclei are adiabatically separated, and the amount of energy necessary to bring this about. More refined investigations of detail are then being applied to other problems of the electronic structure of a term. About a decade ago more than a hundred molecules had already been analysed in this way. Although much experimental work still remains to be done in clearing up the finer details and in providing fuller numerical data, in order that the data relating to the molecules of simple compounds may be completely surveyed, it would seem that the main problems arising in connexion with diatomic molecules have now been entirely cleared up. With polyatomic molecules, unfortunately, we are not yet in this happy position, quite the contrary, in fact. Here I should like to emphasize that hitherto no case exists in which it has been found possible to analyse the electronic bands of a polyatomic molecule in such detail. I do not deny, of course, that some promising beginnings are available (e.g. in papers by Henri, Herzberg, and myself), but that is all. The reasons why triatomic and tetratomic molecules have hitherto defied spectroscopic analysis so persistently in spite of numerous attempts are various.

In the first place, a large number of experimental difficulties have to be overcome. If it is difficult to produce an intense emission spectrum with a diatomic molecule, it is still more so with a polyatomic molecule, where owing to the increased capabilities of rotation and vibration of the molecule its tendency to dissociate is enormously increased. The only conditions of excitation which can be used at all give rise to very feeble intensities (e.g. fluorescence or feeble glow discharge). But as in this very case of the polyatomic molecule great dispersion and great resolving power in the spectrometer are indispensable, we are practically restricted to the use of absorption spectra for reasons of intensity and molecular stability. Here,

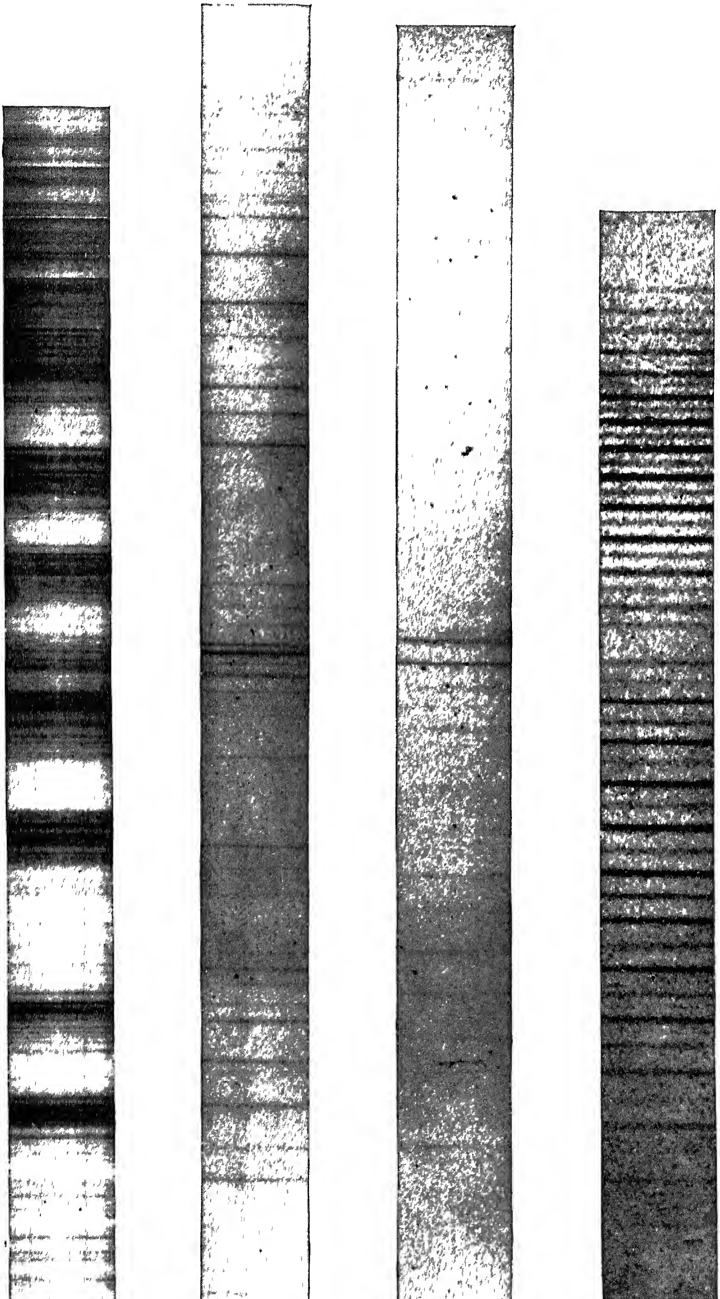
indeed, the first successes have been recorded. Unfortunately however, most molecules absorb only in the remote ultra-violet, and the difficulty of constructing sources giving continuous light of sufficient intensity in these regions has not furthered the success of such investigations.

In addition to these experimental difficulties, which are inherent in the production of spectra, there are many technical difficulties of analysis, quite apart from the difficulty of obtaining adequate resolution of the spectra. In a diatomic molecule we have to determine only *one* moment of inertia and *one* vibrational frequency from the fine structure and the band-head diagram for each electronic state, whereas in a polyatomic molecule of n atoms there are *three* principal moments of inertia and actually $3n - 6$ proper frequencies * for each state. Further, the number of lines and bands in the spectrum increases very rapidly, so that only too frequently it is almost impossible to disentangle them owing to the large number of bands with diffuse edges and irresolvable fine structure. Such results as have been obtained are correspondingly valuable. As an example I give a part of the NO_2 absorption spectrum in the visible region (fig. 1(*a*), Plate I); for further cases, see Henri's fine photographs (Plates IV, V).

Finally, reference may be made to the theoretical difficulties with which we have still to contend. Here I shall not mention the theory of electronic states, and I am not going to discuss dissociation processes which can be traced out spectroscopically. On the other hand I shall in due course discuss the calculation and explanation of the $3n-6$ proper frequencies of a molecule of this type in considerable detail, and shall meanwhile content myself with touching on a few problems of fine structure, i.e. of rotational states. As is well known, the quantization of the simple rotator (Schwarzschild) led to the recognition that the relationships between the lines in the bands of a diatomic molecule must be of quite a simple nature, and this has been justified by experiment in every respect. Once the experimental difficulties in the production of the spectrum and the resolution of the bands are overcome, the classification of *all* the lines of such a spectrum is only a question of the industry and persistence of the investigator. Here really considerable resistance to the efforts of the investigator has been offered only by the many-lined spectrum of hydrogen; this, however, is an

* In long bar-shaped molecules there are $3n-5$ proper frequencies, $n-2$ frequencies then corresponding to so-called double vibrations.

exceptional case, which, moreover, has now been successfully subjected to analysis by a number of workers (Richardson and fellow-workers, Finkelnburg and the author, Weizel, and others). With polyatomic molecules the case is quite different, except in the few favourable instances where the molecule assumes the rotational character of a diatomic molecule owing to the atoms being arranged in a straight line. In the symmetrical top (a molecule with two of its principal moments of inertia equal) the mathematical treatment of the problem is still easy, and difficulty in classifying the series arises only from the profusion of lines in the bands. But as soon as asymmetry, not necessarily of a very marked degree, enters into the molecule, great difficulties arise. The quantization of the "unsymmetrical top" (Kramers, Hund, Dennison, and others) can no longer be carried out exactly, and the method of approximation used shows that a regular recurrence of the lines is no longer to be expected. Experiment, unfortunately, has confirmed this: at present there are *no* definite criteria indicating how the lines of a band are to be associated in series in the case of an unsymmetrical molecule (in which the three principal moments of inertia are unequal). If the lack of symmetry is small, of course, approximate relationships hold good, and these are usually what we obtain from infra-red experiments, where as a rule the frequency curves of lines and not the lines themselves are measured. From these we may calculate approximate values of the moments of inertia, but they are only approximations. As typical examples I may mention the infra-red measurements with water, ammonia, and the methyl halides, to which I shall return later. A further point remains to be noted. The co-ordinates of relative position of a molecule of n atoms require $3n - 6$ different data for their unique determination, but interchange of the *masses* of the atoms is still possible. Determination of the three moments of inertia alone is therefore in *no* case sufficient to establish the structure of a polyatomic molecule definitely. Here we are *invariably* forced to make a priori assumptions. For example, if we assume that in ammonia and in water the distances of the hydrogen atoms from the central atom are really all the same, two moments of inertia (in NH_3, $I_1 = I_2$; in H_2O, $I_1 = I_2 + I_3$) will certainly suffice to determine the internuclear distance and the angle between the valencies, but with the same moments of inertia there always remain two possible ways of arranging the atoms in the molecule, which give a "flat" and a "pointed" molecular model, between which it is impossible to



(a) (b) (c) (d)

Fig 1.—(a) NO_2; (b) H_2O, λ 8230; (c) NH_3, λ 7920; (d) C_2H_2, λ 7886

decide without further data. Fortunately, however, conservation theorems relating to the internuclear distances and the angles between the valencies seem to have a considerable range of validity, so that these difficulties are not of too serious an importance after all.

II. So far I have indicated so many obstacles and made so many negative statements that the impression might readily arise that the analysis of the spectrum of a polyatomic molecule is a thoroughly hopeless business. This, of course, is not the case. It is only necessary to recall that some years back we were confronted with very similar difficulties in the case of diatomic molecules. Then the analysis of the bands was tackled by way of the rotation and rotation-vibration bands (Bjerrum, Kratzer) and success resulted. We shall therefore confine our attention to this type of spectrum meanwhile, i.e. we shall consider the so-called fundamental state * of the molecule only. This limitation simplifies the investigation considerably. So lóng as we confine ourselves to infra-red spectroscopy only, to be sure, not much will be gained. For in that region the experimental methods are such that the separation of the bands is usually insufficient for their fine structure to be disentangled, or the nature of the vibrations associated with individual bands (fundamental frequencies, overtones, combination bands) to be definitely explained owing to the large number of possible combinations of the proper frequencies. Moreover, the short-wave infra-red region below $10\,\mu$, to which most experiments have been confined, by no means suffices for the observation of all the frequencies of the molecule. In the last few years, however, three new and important methods of investigation have come to the assistance of infra-red spectroscopy. The most important of these is the study of Raman spectra; I need not go into special details of its successes.† Here simple spectroscopic apparatus is used to produce a greatly simplified rotation and rotation-vibration spectrum of the molecule on either side of the "exciting" line, usually containing the fundamental frequencies only. The spectrum, however, is certainly not the same as a simplified infra-red absorption spectrum. For example, in the simple molecules H_2, N_2, O_2, &c., no infra-red absorption bands can arise, for reasons of symmetry, whereas the rotational and vibrational bands are clearly exhibited in the

* Ger. *Grundzustand.*

† In connexion with the Raman effect data I have used here and later, reference may be made to the full report by K. W. F. Kohlrausch, *Phys. Zeitschr.*, 32, 385 (1931), where a detailed bibliography down to the end of 1930 is given.

Raman spectrum; they are "infra-red-inactive, Raman-active". On the other hand, the Raman data do not enable us to dispense with data on infra-red absorption. Thus each of these methods will have to supplement the other; it is only through infra-red data that complete explanation of the Raman spectrum will prove possible, and vice versa. Results which have been obtained by bearing this in mind will receive further mention later.

Another important method of investigating molecular structure is the process of molecular interferometry discovered by Debye.* Here the internuclear distances are measured directly from the

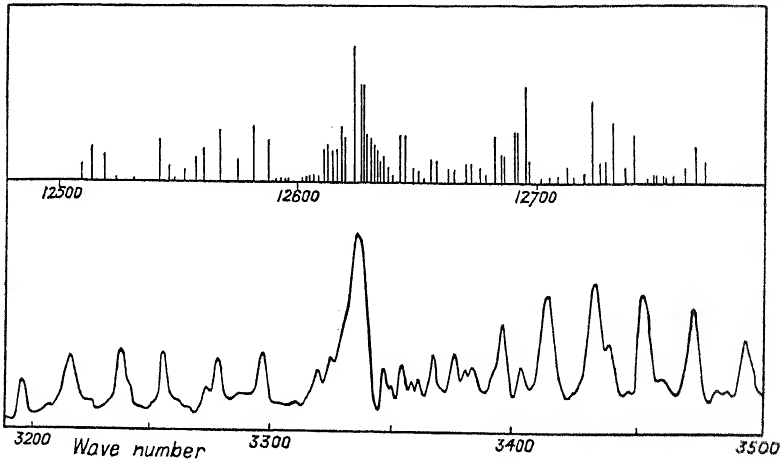


Fig. 2.—Ammonia Bands at 3 μ and 0·1120 μ

diffraction of X-rays (Debye) and electrons (Wierl). Here, of course, I cannot go into the details of the technique or the results of these experiments, but would merely like to emphasize that invaluable service is being done to band spectroscopy by these new methods, for now we can calculate moments of inertia independently of spectroscopic methods and apply them effectively to the solution of problems connected with fine structure. Even in the case of diatomic molecules there are difficulties in disentangling the fine structure of the bands when heavy atoms are involved, and this is true in an increased degree for polyatomic molecules, so that interferometry fits in here as a supplementary method of investigation.

A further extension of the methods of investigation available

* P. Debye, *Ann. d. Physik*, 46, 809 (1915); *Zeitschr. f. Electrochemie* (1930), 613.

is due to *infra-red photography*. Thanks to the new Agfa and Kodak sensitizers it is now possible to photograph absorption spectra with large dispersion very conveniently up to λ 9000 and with some trouble even to beyond 1 μ. Now I have been able to show that the outliers of the rotation-vibration bands reach into this region, even if only in the form of high overtones with but trifling intensity. The advantages, however, are immediately obvious, for now, owing to the possibility of using large concave Rowland gratings, the accuracy and resolution obtained are at once multiplied by several powers of ten as compared with previous infra-red measurements. As this is my own line of research perhaps I may venture to describe it in rather more detail, and at least give you briefly the results which have been obtained hitherto by my fellow-workers and myself. Table I gives a summary of the rotation-vibration bands which have been photographed; these are predominantly concerned with vibrations which are to be ascribed to the O—H, N—H, and C—H bonds. Further details of the notation for the bands and their interpretation will be given later.

TABLE I

Rotation-vibration Bands which have been photographed

NH_3	H_2O	HCN	C_2H_2	CH_4
$\lambda 8800\ (3\nu+\delta)$ $\lambda 7920\ (4\nu)$ $\lambda 6474\ (5\nu)$	$\lambda 9440\ (3\nu_1)$ $\lambda 9050\ (2\nu_1+\nu_2)$ $\lambda 8230\ (3\nu_1+\delta)$ $\lambda 7230\ (4\nu_1)$ $\lambda 6970\ (3\nu_1+\nu_2)$ $\lambda 6500\ (4\nu_1+\delta)$ $\lambda 5910\ (5\nu)$	$\lambda 7912\ (4\nu_1)$ $\lambda 8563\ (3\nu_1+\nu_2)$	$\lambda 7886\ (3\nu_3+\nu_2)$ $\lambda 8622\ (3\nu_3+\nu_1)$	$\lambda 8860$
I_1 $2{\cdot}80.10^{-40}$ I_2 $3{\cdot}49$ I_3	$0{\cdot}98 . 10^{-40}$ $1{\cdot}80$ $2{\cdot}80$	$18{\cdot}79 . 10^{-40}$	$23{\cdot}509 . 10^{-40}$ $(0{\cdot}5)$	$5{\cdot}17.10^{-40}$

The first molecule to be successfully investigated was ammonia;* it was found possible to photograph three bands, λ 8800 $(3\nu + \delta)$, λ 7920 (4ν) (fig. 1(*c*)), and λ 6470 (5ν). Fig. 2 gives a comparison between the fundamental band at 3 μ (ν) investigated very thoroughly by Barker and Stinchcomb † and its third overtone (4ν) photo-

* R. Mecke, *Phys. Zeitschr.*, **30**, 907 (1929); R. M. Badger and R. Mecke, *Zeitschr. f. phys. Chemie*, **5**, 333 (1929); R. M. Badger, *Phys. Rev.*, **35**, 1038 (1930).

† G. A. Stinchcomb and E. F. Barker, *Phys. Rev.*, **33**, 305 (1929).

graphed by us at λ 7920, which should have the same structure; this was found to be the case. Both bands are shown on the same frequency scale. This comparison shows quite typically how even with very accurate grating experiments in the infra-red statistical frequency curves are still obtained, and how much more complicated the fine structure of the ammonia bands is than the infra-red investigations have hitherto led us to suppose. The theory of a molecule of this type, however, entirely leads one to expect this kind of structure. The ammonia pyramid is thought of as a symmetrical molecular model, whereas unsymmetrical features make themselves unpleasantly noticeable in the structure of the bands photographed. Hence the moment of inertia calculation giving the molecular data 0·977 Å. for N—H, 1·43 Å. for H—H, and 0·517 Å. for h (the height of the pyramid) is to be regarded as only approximate. Here, however, fresh experiments are being made and will be reported on in due course.

Our investigation of the absorption of acetylene * has had an unexpectedly successful result. The two bands photographed at λ 7886 (fig. 1 (*d*), Plate I) and λ 8620 exhibited a remarkably simple structure, namely that of a diatomic molecule; that is, the four atoms must lie in a straight line. A slight bending of the H—C—C—H bar, however, is manifested at λ 7956 by the appearance of feeble subsidiary bands on either side of the main band. Nevertheless a very exact determination of the moment of inertia was possible, leading to the distances 1·08 Å. for C—H (assumed known, see above) and 1·19 Å. for C$\equiv$C. In addition the bands exhibited the feature of alternating intensities which years ago I discovered with symmetrical diatomic molecules. We were even able to make exact measurements of intensity, and found that the intensity ratio is accurately given by $1:3 \pm 0{\cdot}1$ (fig. 3, Plate II); at the same time we were able to test the intensity formulæ for "diatomic" molecules.† The nuclear spin of hydrogen is thereby definitely established by spectroscopy as $\frac{1}{2}$.‡ Badger and Binder §

* K. Hedfeld and R. Mecke, *Zeitschr. f. Physik*, 64, 151 (1930).

† W. H. T. Childs and R. Mecke, *Zeitschr. f. Physik*, 64, 162 (1930).

‡ Hitherto this value has been obtained *solely* from the behaviour of the specific heat of hydrogen. Owing to its short series and absence of knowledge as to the temperature at which it is excited, the many-lined spectrum of hydrogen is not at all suited for this determination. In addition, it was questioned whether the intensity ratio is really exactly equal to 1 : 3.

§ R. M. Badger and J. L. Binder, *Phys. Rev.*, 37, 800 (1931).

PLATE II

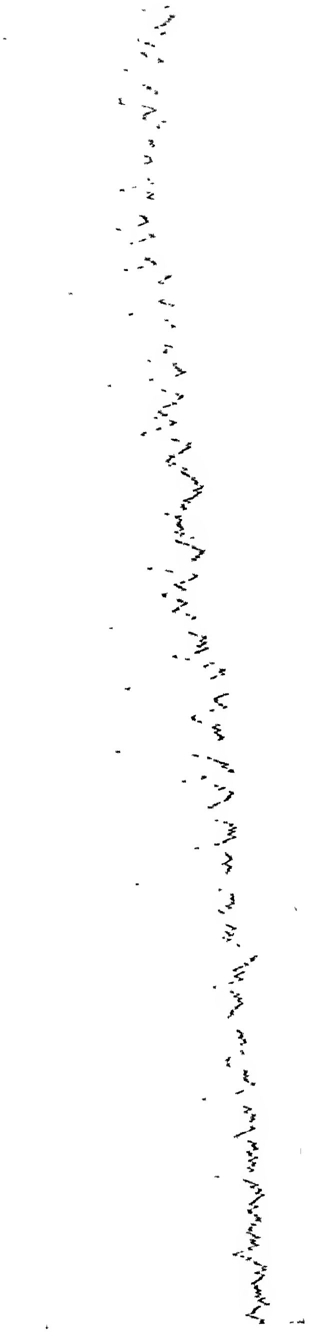


Fig 3.—Alternating Intensities in C_2H_2, λ 7886

have carried out similar investigations with the hydrocyanic acid molecule (HCN), which is also linear, with dimensions 1·08 Å. for C—H (assumed known), and 1·15 Å. for C≡N. Here, of course, the bands (λ 7912 and λ 8563) do not exhibit alternating intensities. With these two molecules, however, the group of "isosteric" compounds N_2, CO, C_2H_2, and HCN (14 electrons) is completed, and the fact is established * that isosterism gives rise to considerable spectroscopic similarity also; more details will be given later (see Table V, p. 38).

The greatest number of bands was photographed in the case of water vapour † (fig. 1 (*b*), Plate I), namely, not less than five, and if we count in the atmospheric lines in the sun's spectrum a few others have to be added. A very satisfactory subsidiary result is that *all* the atmospheric lines in the sun's spectrum are to be ascribed to water vapour or oxygen.† As the molecule is unsymmetrical, the analysis of the fine structure involves considerable difficulties, for the reasons mentioned above. The investigations, however, led to an approximate evaluation of the moments of inertia,‡ giving 0·94 Å. for O—H and 1·43 Å. for H—H. Further, the third proper frequency which hitherto had not been found in the infrared was obtained photographically.

The spectrum of methane is being investigated at the moment, but I do not propose to give any details here. In methane, curiously enough, very marked asymmetry is displayed in the band at λ 8860, which again makes the analysis much more difficult. For all these molecules, moreover, it has been found possible, as we shall see in a moment, to obtain the proper frequencies and their possible combinations by means of these photographic investigations in conjunction with infra-red and Raman data. Even if the application of infra-red photography to rotation-vibration spectra remains confined to the X—H vibrations only, I take an entirely optimistic view of the advances to be achieved by this method of investigation, the advantage of which is predominantly due to the use of large dispersion, and which will later play a great part in the solution of problems of fine structure.

III. In what follows I should like to narrow down the scope of my remarks, and in the first place I shall now leave those problems

* R. Mecke, *Trans. Farad. Soc.* (Liverpool meeting, 1931).

† R. Mecke, *Phys. Zeitschr.*, **30**, 907 (1929); *Zeitschr. f. wiss. Photographie* (Congress volume, Dresden, 1931).

‡ R. Mecke, *Trans. Farad. Soc.*, **26**, 213 (1930).

of fine structure which have not yet been mastered with certainty either on the experimental or the theoretical side. Further, I shall make no reference to the properties of symmetry of a molecule which are so important both in theory and practice, i.e. I shall refrain from discussing the questions under what conditions a band is missing from the infra-red absorption spectrum (so-called " inactive " vibration), when combination frequencies are to be expected to occur in that region, and what frequencies may occur in the Raman spectrum. These matters will be dealt with by Dr. Placzek in another paper (p. 65). The problem I shall consider here is simply whether it is possible on the basis of the experimental data hitherto available to evaluate the *magnitudes of the proper frequencies of a polyatomic molecule* with any certainty and at the same time to form a clear idea as to the nature of the vibrations of such molecules. The question is a very important one, not only in view of the hope of explaining infra-red bands and Raman frequencies, but more particularly with reference to the possibility of applying these to chemical problems.

It is only when we are *definitely* in a position to *determine and classify proper frequencies* that it will be possible to advance structural chemistry by purely spectroscopic means and thereby assist the chemist in establishing the structural formulæ he deduces from the chemistry of reactions, or possibly improve on his formulæ. To me the solution of this problem seems the *principal object* of the spectroscopic investigation of polyatomic molecules at the present time, and I am convinced that the goal is entirely within reach.

To indicate the way along which progress will have to be made, I shall recall some results in the band spectroscopy of diatomic molecules. These will show that some of the molecular data obtained from diatomic substances turn up again almost unaltered in more complicated substances; that is, we attempt—just as the chemist does—to build up a polyatomic molecule out of " standardized " diatomic constituents.

In the first place, the internuclear distance is one of these additive quantities. Fig. 4 shows how this distance alters quite regularly, e.g. in the diatomic hydrides, and in particular how the shells of electrons are built up, discontinuities always occurring at the inert gases. I cannot go into details here. The internuclear distance, however, remains very much the same if we pass from unsaturated radicals to saturated compounds, e.g. from CH, NH, OH to CH_4, NH_3, H_2O, except that a small diminution by about five or ten

per cent indicates the "hardening" of the molecule, which is entirely what one would expect from chemistry (see Table II). What we have stated here for the hydrogen compounds is also true for other compounds; for example, in the carbon-nitrogen-oxygen compounds

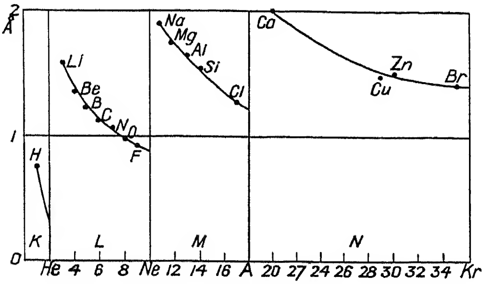


Fig. 4

the internuclear distance is 1·5 Å. for the various types of *single* bond, 1·23 Å. for the *double* bond, and 1·12 Å. for the *triple* bond (with an unexpectedly small range of variation, see Table III). This result is of importance, for it enables us to obtain unknown internuclear distances or angles between valencies * in polyatomic molecules from moments of inertia found by spectroscopic means or from interferometric measurements (Debye).

TABLE II

Internuclear Distances and Nuclear Frequencies of Saturated and Unsaturated Hydrides

XH_n	ν	r	XH	ν	r
CH_4	2915	1·08	CH	2815	1·13
NH_3	3336	0·98	NH	3085	1·07
OH_2	3750	0·94	OH	3570	0·97
FH_1	3962	0·92	FH	3962	0·92

Another quantity characteristic of the molecule is the nuclear frequency of a diatomic compound, for this enables us to determine the nature of the valency bond *uniquely*. I begin with the frequency

* See e.g. the question of the spreading of the valencies in the halogen derivatives of methane, P. Debye, *Zeitschr. f. Electrochemie*, 1930, p. 612; L. Bewilogua, *Phys. Zeitschr.*, 32, 265 (1931).

curve for the diatomic oxides (fig. 5). We see how with an advance through the periodic system every electron added at first raises the nuclear frequency and hence tends to strengthen the bond, until a maximum is reached in CO (or SiO). The next electron added on in N (or P) may also have a hardening effect, but no longer in the fundamental state as in the preceding oxides; on the contrary it is only the next higher state of electronic excitation that has this surprisingly large stability. In NO in the fundamental state, however, the bond is loosened owing to the new electron attracting another electron out of the binding shell, and this loosening goes on through oxygen to the next inert gas, where the minimum zero is again

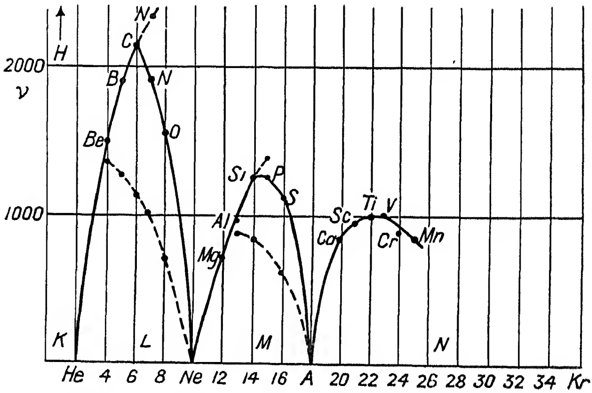


Fig. 5.—Nuclear Frequency Curve for Diatomic Oxides

reached; here no electron can form a binding shell with oxygen. This example is chiefly meant to show how we may draw definite conclusions about the nature of the binding from the magnitude of the nuclear frequency. Thus it may easily be shown that in the various electronic states of a diatomic molecule the nature of the linkage varies, i.e. the number of binding electrons varies from level to level. This is clearly exhibited by a sudden jump in the nuclear frequency. In fig. 5 some of these stages of excitation are indicated by the dotted curve, probably corresponding to a single bond. A further example is the ultra-violet absorption of nitrogen and oxygen, where as a result of light absorption the triple N N bond and the double O=O bond are transformed respectively into a double bond ($\dot{N}=\dot{N}$) and a single bond ($\dot{O}-\dot{O}$) with "upright" valencies, the change being manifested by a very sudden fall of

the nuclear frequencies from 2360 and 1576 to 1680 and 708. In the diatomic carbon-nitrogen-oxygen compounds which we have already mentioned, *statistical* investigation of the various states of excitation shows that the values are grouped very closely about the average values 2200 for X≡X, 1650 for X=X, and 1025 for X—X (Table III). But these considerations, of which only a small part can be reproduced here, lead necessarily to an *extension or modification* of our previous conception of valency. We are now forced to draw a sharp distinction between the *valency* of an *atom* and the *character of the binding* in a *molecule*. Thus e.g. the spectroscopic resemblance between carbon monoxide and nitrogen (which extends to minute details, whereas there are wide differences between carbon

TABLE III

Mean Values of the Characteristic Molecular Data ν, r, and k for various carbon-oxygen-nitrogen compounds

	ν	r	k
X≡X	2200 ± 120	1·12 ± 0·03	(79 ± 6)V (1800 Cal.)
X=X	1650 ± 140	1·23 ± 0·04	(54 ± 6)V (1250 Cal.)
X—X	1025 ± 180	1·50 ± 0·05	(27 ± 7)V (600 Cal.)
X—H	2900 — 3600	1·13 — 0·92	2·4(Z + 1)V (55·5 Cal.)

monoxide and the carbonyl =C=O group) forces us to assume that carbon monoxide contains a triple bond (C≡O); this assumption, moreover, is supported to a considerable extent by other similarities, both physical (isosterism) and chemical (the parachor, heat of dissociation, &c.). To exhibit the *character of the binding* in the chemical structural formula I propose that in place of the dash between the symbols of the elements, which has hitherto denoted merely the valency of the *atom*, the *number of binding electrons* should always be inserted. For example, carbon monoxide would be denoted by C(2 + 4)O; that is, the two valency electrons of the carbon atom together with the four valency electrons of the oxygen atom are supposed to give rise to the characteristics of the triple bond; at the same time this avoids the difficulties of assuming the bivalency of carbon in a stable molecule. For the three electronic levels of NO with nuclear frequencies 2345, 1891, and 1030 we may then analogously write N(5 + 2)O, N(3 + 2)O,

and N(1 + 2)O. It remains for further experiments to elucidate the term characteristics of these electrons (π and σ electrons).

IV. After these somewhat rambling remarks, which, however, I consider of fundamental importance, I return to the question of an additive quantity associated with the bond which will enable us to calculate the proper frequencies of polyatomic molecules. The proper frequency of a bond between two atoms is not itself suited to this purpose, but in analogy with the modulus of elasticity in mechanics we shall introduce as the *binding constant* the amount of work required to double the internuclear distance on the assumption that Hooke's law of elasticity is strictly followed. This is at once

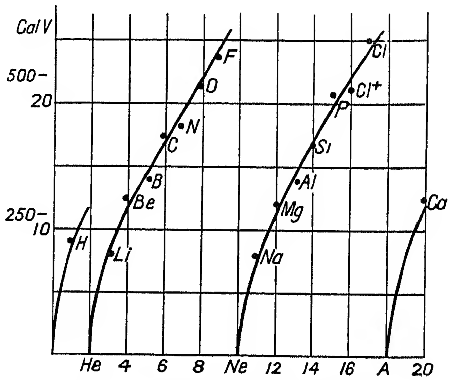


Fig. 6.—Binding Constants for Hydrides

obtained from the expression for the potential of a bond of this type (a so-called harmonic bond),

$$P = k(\Delta r/r)^2, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and for a diatomic molecule is readily calculated from the nuclear frequency ω and the moment of inertia μr^2;

$$2\pi\omega = \sqrt{2k/\mu r^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

I shall illustrate the importance of this binding constant k by means of one or two examples. Fig. 6 gives a graphical representation of this quantity for the diatomic hydrides. Beginning with zero at the inert gases the curve rises regularly in each period of the elements. A curvature at the first element in each (H, Li, Na) shows that here s-electrons enter into the bond; subsequently, where only p-electrons are involved, the increase in the strength of the binding is almost linear, so that the k-constant may be

approximately expressed by the formula (of course quite empirical) $k = 2{\cdot}4\ (Z' + 2)$ volts or $55{\cdot}5\ (Z' + 2)$ Cal./mol, where Z' means the total number of the *outer* electrons. Here, then, all the outer electrons have a bond-strengthening effect; that is, the character of the single X—H linkage arises from the fact that the *hydrogen electron is taken up and treated exactly as a member of the family of electrons of the other element*. Further interesting details cannot be discussed here. In the carbon-nitrogen-oxygen compounds the values for the single, double, and triple bonds are also grouped very closely about the numerical values 27V, 54V, and 77V (Table III) and to a fairly good approximation are in the ratio of 1 : 2 : 3. We see that they are considerably greater than in the case of the hydrides. Of special importance in what follows, however, is the

TABLE IV

Hydrogen Halides

H—X	ν	r	k	
H—F	3962	0·92	23·3V	
H—Cl	↑ 2995	↓ 1·28	24·5V	
H—Br	2560	1·42	24·0V	
H—I	2230	1·62	24·0V	24·0V
H—H	4250	0·75	9·3V	

fact that this *binding energy is to a great extent constant for elements which are chemically alike*, i.e. for those which stand vertically below one another in the various groups of the periodic table and have the same number of valency electrons. As an example I shall first bring forward the hydrogen halides (Table IV), in which, as we see, k remains constant (24·0V), although nuclear frequency and internuclear distance vary considerably. In view of the greater electron affinity, however, the value is considerably greater than that corresponding to the H_2 molecule (9·3V), where only two K electrons are involved in the bond.

In Table V polyatomic molecules are taken into account, and values of the binding constant are given for triple, double, and single bonds between molecules with 10, 12, or 14 outer electrons. The constancy of the quantity is again obvious. Table VI gives data for the methyl halides of type (H_3C)—X, i.e. the frequencies which are characteristic of that bond alone and from which (as we shall

show later) the k-values may be calculated. Here again the stancy is maintained pretty well.

TABLE V

Binding Constants for the X≡X, X=X, and X—X Bonds

10 Valency Electrons

X≡X	ν	r	k	
N≡N	2360	1·10	85V	
C≡O	2162	1·15	77V	
(HC)≡N	2090	1·15	75V	
(HC)≡(CH)	1975	1·19	70V	77V

12 Valency Electrons

X=X	ν	r	k	
O=O	1577	1·20	53V	
$H_2C=CH_2$	1623 *	(1·30) †	54V	
$H_2C=O$	1770 *	(1·25) †	56V	55V

14 Valency Electrons

X—X	ν	r	k	
F—F	1140	1·27	37	
Cl—Cl	560	1·98	40	
Br—Br	327	2·28	40	
I—I	214	2·66	38	
I—Cl	383	2·31	39	38V

TABLE VI

Methyl Halides

(H_3C)—X	ν	r	k	
(H_3C)—F	1050	1·43	32V	
(H_3C)—Cl	↑ 730	↓ (1·85) †	31V	
(H_3C)—Br	595 *	(2·25) †	36V	
(H_3C)—I	522 *	?	—	33V
(H_3C)—H	2915	1·08	18·4V	

* Raman experiments. † Interferometric experiments.

TABLE VII *

Chlorine Derivatives of Methane

$(H_xC)—Cl_y$	ν	r	k
$(H_3C)—Cl$	730	1·85	31V
$(H_2C)—Cl_2$	700	1·94	40V
$(HC)—Cl_3$	666	1·86	50V
$(C)—Cl_4$	455	1·83	45V
H—Cl	2995	1·28	24·5V

TABLE VIII *

Tetrachlorides ("Inactive" Vibration)

XCl_4	ν	r	k	
CCl_4	455	1·83	45V	
$SiCl_4$	422	2·01	46V	
$TiCl_4$	386	2·21	47V	
$SnCl_4$	367	2·33	46V	46V
CH_4	2915	1·08	18·4V	

In the case of (H_3C)—I, for example, where the internuclear distance has not been obtained either spectroscopically or by interferometry, its value may be calculated to be 2·50 Å. The greater electron affinity of the halogens is again shown by comparison with methane ((H_3C)—H), for which the binding constant is only 18·4V. The same conclusions are obtained by clorinating methane in stages until carbon tetrachloride is produced (Table VII). Here the constancy is not so well marked; the value of *k* steadily increases as the number of chlorine atoms does, as the latter owing to their electron affinities also exert a small attraction on one another and in addition there is a spreading of the angles between the valencies which is not taken into account here. If, however, we consider a number of different tetrachlorides, in which the *configuration* of the molecule remains unaltered (Table VIII), we again obtain

* Raman and interferometric experiments.

remarkable constancy. The value, to be sure, is greater than for the monochlorides and considerably greater than that for methane, but the effect of the central atom and its internuclear distance is obviously very trifling. These examples will suffice in the meantime to show that in the "rigidity" of a chemical valency bond defined in this way we have really found a good criterion of the character of the binding and that this quantity is to a considerable extent an additive property, i.e. that it retains practically the same value even in complicated compounds. These results now enable us to calculate a large number of proper frequencies of polyatomic molecules with an adequate degree of certainty from the internuclear distance and the rigidity of a valency bond.

V. In order to express the nature of the vibrations associated with a proper frequency I proposed more than a year ago that they should be classified under the headings of the so-called *valency vibrations* and *deformation vibrations*.* In what follows I shall briefly show that this distinction is always possible. We start off from the quite simple idea of a valency bond as a thin elastic rod, without, however, losing sight of the existence of binding shells of electrons which really maintain the cohesion of the molecule. A rod of this kind is in the first place capable of extension, and we shall actually define this elastic extensibility by means of our binding constant k. In addition, however, the rod may be bent, and in general the flexural elasticity must be expressed by *two* binding constants, one of which (b) corresponds to the bending force in the direction of greatest constraint, and the other (b') to the bending force in the direction of least constraint. This means nothing more than that the flexural vibration of a rod is in general represented by a Lissajous figure, and may always be decomposed into two proper vibrations at right angles to one another—in the directions of least and greatest constraint. If we meanwhile ignore ring compounds (these, however, offer no difficulty in theory whatever), it follows at once that a "rod molecule" of this kind with n atoms must always possess $n - 1$ "rods" and hence also $n - 1$ extensional vibrations (valency frequencies) and $2n - 5$ flexural vibrations (deformation frequencies). We see in addition that in building up the molecule every valency dash added, i.e. every new atom attached, must always give rise to three new frequencies, one valency vibration and two deformation vibrations.

* R. Mecke, *Zeitschr. f. Electrochemie* (1930), p. 589 (Bunsen commemoration, Heidelberg).

So much for the simple mechanical conceptions.* I must, however, issue a warning against attempts to narrow them down too much by adding finer details. The proper frequencies are calculated by the well-known method of small oscillations, suitable normal co-ordinates being used; here it must always be borne in mind that we are using an approximate process. In accordance with the above conceptions, then, we assume the following simple expression for the potential, containing $3n - 3$ molecular constants:

$$P = \sum_{i}^{n-1} [k_i \left(\frac{\Delta r}{r}\right)^2 + b_i \Delta\phi^2 + b_i' \Delta\psi^2], \quad . \quad . \quad . \quad (3)$$

where $\Delta\phi$ and $\Delta\psi$ are angles of bending. As, however, the vibration must involve no transference of resultant linear or angular momentum, the number of independent constants is reduced to $3n - 6$, and the solution gives $3n - 6$ proper frequencies. In the most general case, of course, these are functions of *all* the masses present in the molecule, *all* the internuclear distances, and *all* the values of k_i and b_i (b_i'): $\omega_k = F(m_i, r_i, k_i, b_i, b_i')$. Practical experience has shown, however, that the extensional elasticity of the bond is about ten times as great as the flexural elasticity. In fact, the possibility of the existence of a "valency dash" and its essential nature directly depend on the fact that its quasi-elastic stress ellipsoid has its axes in the ratio of 1 : 10. If this is not the case the possibility of drawing "valency dashes" between two atoms immediately ceases to exist. Moreover, in the determination of the values of k and b we have a *purely spectroscopic criterion* of the correctness of a chemical structural formula. In this connexion, therefore, band spectroscopy becomes of increased interest in connexion with stereochemistry, especially that of cyclic compounds (e.g. the benzene ring).

Making the above assumptions we may always expand the function giving the proper frequencies in rapidly convergent power series

* A similar conception forms the basis of Andrews' views (*Phys. Rev.*, **36**, 544 (1930)), and led him to the construction of mechanical molecular models. He does not, however, make the sharp distinction between valency vibrations and deformation vibrations. The essential feature of my discussion of the problem, namely, the expression of this distinction by setting up vibration diagrams and by calculation, is therefore absent from his treatment. Further, in order to avoid confusion, I would emphasize that his binding constant k is not identical with mine. In Andrews' paper it has the dimensions dyne/cm., hitherto usual, but is in no way a criterion of the nature of the bond, as it takes no account of the internuclear distance. See also K. W. F. Kohlrausch (*Phys. Zeitschr.*, **32**, 385 (1931)), who gives yet another definition of the strength of a bond.

in b_i/k_i. Accordingly we usually remain within the realm of validity of the method of small oscillations even if we neglect the first term in b/k, i.e. this *first* approximation gives a number of proper frequencies $(n - 1)$ which are functions of the quantities k_i only, and $2n - 5$ which to a first approximation depend on the quantities $b_i(b_i')$ only. According to our definition we call the former valency vibrations and the latter deformation vibrations. This approximation process, which simplifies the otherwise complicated calculation very considerably, also leads us to an easy graphical interpretation of the valency and deformation vibrations. For the expansion in series and breaking off at the first term merely mean that for the *terminal* atoms, i.e. for those attached by only *one* valency bond, the vibration is in the direction of the valency dash for the valency frequency, and at right angles to it for the deformation frequency. For the central atoms, of course, this statement is not true. If, however, the molecule (radical) has an axis of symmetry, e.g. has several atoms of the same kind attached to a central atom (NH_3, —CH_3, OH_2) we can speak of a π-vibration or a σ-vibration, according as this central atom vibrates parallel to or at right angles to the axis of symmetry. In other cases of symmetry we shall in addition have to discriminate between symmetric and antisymmetric vibrations. I should therefore like to propose the following notation: if we make no attempt to classify the proper frequencies, we shall denote them by ω_i, in accordance with the usual terminology for diatomic molecules. If, however, we make use of the classification into valency frequencies and deformation frequencies explained above, we shall denote them by ν_i and δ_i, and if further classification is required we shall subdivide these into π and σ (or s and a) vibrations. This notation should meanwhile suffice in almost all cases.

A further important simplification of the calculation of proper frequencies may be brought about if we give up the attempt to obtain a complete solution and concentrate on particularly interesting proper frequencies by considering groups of atoms (radicals) as a whole. To begin with, we can usually make considerable use of the advantage of a great difference in mass. For example, the —(CH_n) radical may always be regarded as a unit for the X—C vibrations, as in the *common* vibration of the C and H atoms the latter affect the frequency but slightly. On the other hand, in the so-called C—H vibration e.g. the group (Cl_3C) in chloroform ($HCCl_3$) may be regarded as a unit, for the C atom has little effect, and the Cl atoms practically none at all, on this vibration. In this way we

readily obtain "diatomic" molecules (see Tables IX–XI). In contradistinction to "genuine" diatomic molecules, however, these molecules exhibit deformation vibrations as well. Now the way in which these flexural vibrations of the valency degenerate into a double vibration in the case where the axis of symmetry of the

TABLE IX

Valency Vibrations of "Diatomic" Halogen Derivatives (Raman lines)

	$(X_3)-(CH)$	$X-(CH_3)$	$X-(C_6H_5)$
Cl	666	730	420
Br	538	595	317
I	—	522	266

TABLE X

Valency Vibrations and Deformation Vibrations of "Diatomic" Molecules

$N\equiv(CH)$	2090		710	
$O=(CH_2)$	1768	1020		920
$F-(CH_3)$	1048		1200	
$(H_3C)-(CN)$	925		375	
$(H_3C)-(C_6H_5)$	1005	345		215

TABLE XI

"Triatomic" Cyanogen Compounds

	X—C	C—N	X—C—N
H—C—N	3290	2090	710
(H_5C_6)—C—N	1003	2237	?
(H_3C)—C—N	916	2250	376

molecule coincides with the valency dash, but split up into two proper frequencies in the case where the molecule is asymmetric (H_2CO, $C_6H_5CH_3$), is very characteristic. A few typical examples are given in Table X, in which the valency frequency is also given. From these the values of k and b are of course obtained only approximately, as the frequencies are naturally somewhat affected by the other values for k and b. Further examples of valency vibra-

tions for diatomic molecules and analogous results for triatomic molecules (cyanogen compounds) are given in Tables V, IX, and XI.

A number of *identical* atoms (or radicals) attached to a central atom may likewise be regarded as a group. If by α we denote the angle made by one of these "n-ply split valencies" with the axis of symmetry, a molecule e.g. of type Z_m—X—Y_n vibrates in its *two* $\nu(\pi)$ frequencies like a linear Z—X—Y molecule, except that instead of k_y and Y it has a binding constant $k_y n \cos^2\alpha$ and an apparent mass $Y_n \cos^2\alpha$, and similarly for Z_m. Then the two $\nu(\pi)$ frequencies are calculated from the somewhat complicated-looking formula

$$(2\pi\nu_\pi)^2 = \left(\frac{k}{\mu r^2}\right)_z + \left(\frac{k}{\mu r^2}\right)_y \pm \sqrt{\left[\left(\frac{k}{\mu r^2}\right)_z - \left(\frac{k}{\mu r^2}\right)_y\right]^2 + \frac{4k_z k_y mn \cos^2\alpha_z \cos^2\alpha_y}{r_z^2 r_y^2 X^2}}, \quad . \quad (4)$$

in which the two "reduced" masses μ_z and μ_y are defined by

$$\frac{1}{\mu_z} = \frac{1}{Z} + \frac{m\cos^2\alpha_z}{X} \quad \text{and} \quad \frac{1}{\mu_y} = \frac{1}{Y} + \frac{n\cos^2\alpha_y}{X}. \quad . \quad (5)$$

A similar expression also holds for the corresponding deformation vibration of this "triatomic" molecule, except that $\cos^2\alpha$ is replaced by $\sin^2\alpha$.

In this way it is easy to identify the proper frequencies of the various halogen derivatives of methane; these are summarized—so far as Raman and infra-red data are available—in Table XII. From these quantities it should not be difficult to estimate the hitherto missing values for the iodine derivatives.

The $\nu(\sigma)$ vibration of a group of atoms may similarly be calculated from a bent triatomic molecule. In this way we obtain e.g. for molecules such as chloroform and methyl chloride (Z—X—Y_3) the *one* valency vibration (double vibration)

$$2\pi\nu_\sigma = \sqrt{\frac{2k_y}{r_y^2}\left[\frac{1}{Y} + \frac{3/2\sin^2\alpha}{X}\right]}, \quad . \quad . \quad . \quad . \quad (6)$$

and for a molecule of the type of methylene chloride (Z_2—X—Y_2) the *two* $\nu(\sigma)$ frequencies

$$2\pi\nu_\sigma = \sqrt{\frac{2k_z}{r_z^2}\left(\frac{1}{Z} + \frac{2\sin^2\alpha_z}{X}\right)}, \quad 2\pi\nu_\sigma = \sqrt{\frac{2k_y}{r_y^2}\left(\frac{1}{Y} + \frac{2\sin^2\alpha_y}{X}\right)}. \quad (7)$$

TABLE XII

"Triatomic" Halogen Derivatives

Valency Vibration $C—H_z$

	X_3-C-H		X_2-C-H_2		$X-C-H_3$
Cl	3025	⟵	2988	⟵	2967
Br	3025		2988		2967
I	—		2970		2971

Valency Vibration $X_y—C$

	X_3-C-H		X_2-C-H_2		$X-C-H_3$
Cl	666	⟶	700	⟶	730 ↑
Br	538		576		595
I	—		487		522

Deformation Vibration $X—C—H$

	X_3-C-H		X_2-C-H_2		$X-C-H_3$
Cl	1218	⟵	1027?	⟵	1020 ↑
Br	1142		1096		957
I	—		1125		885

TABLE XIII

Constancy of the $\nu(\sigma)$ Vibration

$(H—C)—Cl_3$ $(Cl—C)—Cl_3$	761 776	$(H_2—C)—Cl_2$ $(Cl_2—C)—Cl_2$	734 776
$(H—C)—Br_3$ $(Br—C)—Br_3$	654 667	$(H_2—C)—Br_2$ $(Br_2—C)—Br_2$	634 667
$(H—C)—Cl_3$ $(HOC—C)—Cl_3$	761 732	$(O—S)—Cl_2$ $(S—S)—Cl_2$	451 443

As in all these $\nu(\sigma)$ vibrations the other valency bond is subject to "bending" only, its binding constant and the mass of the outer atom do not appear in the formulæ in this approximation, so that the frequency is largely independent of these bonds. Table XIII gives a few examples in which the $\nu(\sigma)$ frequency actually does

TABLE XIV

Bent Molecule $X\langle^{H}_{H}$

	$\nu(\sigma)$	$\nu(\pi)$	$\delta(\pi)$
$—CH_2$	3060	2980	1450
$—HN_2$	3360	3260	?
OH_2	3750	3650	1600
SH_2	2685	2615	1180

TABLE XV

Bent Molecule $(H_2C)\langle^{X}_{X}$

	$\nu(\sigma)$	$\nu(\pi)$	$\delta(\pi)$
$(H_2C)Cl_2$	734	697	283
$(H_2C)Br_2$	634	578	178
$(H_2C)I_2$	573	487	119

TABLE XVI

Molecular Data for the Methyl Halides

	$(H_3C)—F$	$(H_3C)—Cl$	$(H_3C)—Br$	$(H_3C)—I$
I_1	4·81	4·70	4·73	$4·71 \cdot 10^{-40}$
I_2	33·2	(81)	(170)	—
H—H	1·71	1·69	1·70	$1·70 \cdot 10^{-8}$
C—H	1·05	1·04	1·04	$1·04 \cdot 10^{-8}$
X—C	1·42	(1·85)	(2·3)	$(2·5 \cdot 10^{-8})$
$\nu(\sigma)$	2987	3047	3061	3074
$\nu(\pi, s)$	2965	2967	2972	2971
$\nu(\pi, a)$	1048	732	595 (Ra)	522 (Ra)
$\delta(\pi)$	1476	1460	1450	1445
$\delta(\sigma, s)$	1476	1355	1305	1252
$\delta(\sigma, a)$	1200	1020	957	885
k_X	32V	31V	36V	—
k_H	19V	19V	19V	19V

remain remarkably constant in spite of great difference of mass and character of binding (see Tables VI, VII, pp. 38, 39). Hence for $\nu(\sigma)$ in radicals like $—CH_2$, $—CH_3$, $—NH_2$, $—NO_2$, &c., it matters very

TABLE XVII

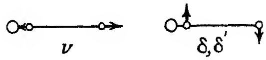
Molecular Models

Type	Proper Vibrations	Examples
1. $X—Y$	$\omega_i = 3$ ν, δ, δ'	Halogen derivatives: $X—(CH_3)$, $X—(C_6H_5)$, $H—(CX_3)$; $(C_6H_5)—(CH_3)$; $(H_2C){=}O$, $H(CN)$.
2. $Z—X—Y$ (straight) HCN type	$\omega_i = 4$ $\nu(s)$; $\nu(a)$; δ (double)	HCN, $(CH_3)CN$, $(C_6H_5)CN$; $HC(X_3)$, $H_2C(X_2)$, H_3CX (where X represents a halogen); CO_2, CS_2, COS, N_2O.
3. $Y\diagup^{X}\diagdown Y$ (bent) Water type	$\omega_i = 3$ $\nu(\pi)$; $\nu(\sigma)$; $\delta(\pi)$	H_2O, $—NH_2$, $=CH_2$, SO_2, $(H_2C)R_2$, R_2O (where R represents a radical).
4. $Y—X—X—Y$ (straight) Acetylene type	$\omega_i = 7$ $\nu_1(s)$; $\nu_2(s)$; $\nu(a)$; $\delta(s)$, $\delta(\alpha)$ (double)	C_2H_n, H_2O_2, N_2H_4, $(CN)_2$; CC_2C_2C (benzene ring) $R(C_6H_4)R$ (p-di-derivative).
5. $Z—X\langle^{Y}_{Y}$ (plane) Formaldehyde type	$\omega_i = 6$ $\nu(\pi, s)$; $\nu(\pi, a)$; $\nu(\sigma)$; $\delta(\pi)$; $\delta(\sigma)$; $\delta'(\sigma)$	H_2CO, Cl_2CO, Cl_2SO, Cl_2S_2, $(CH_3)_2CO$, $(CH_2)NO_2$, $(C_6H_5)NO_2$, $—CO_3$, SO_3.
6. $X\langle\begin{smallmatrix}Y\\Y\\Y\end{smallmatrix}$ (pyramidal) Ammonia type	$\omega_i = 6$ $\nu(\pi)$; $\nu(\sigma)$ (double) $\delta(\pi)$; $\delta(\sigma)$ (double)	NH_3, $—CH_3$, AsH_3, PH_3, $(HC)Cl_3$, $(HC)Br_3$, PCl_3, $AsCl_3$, $SbCl_3$, $BiCl_3$, $AlCl_3$, NCl_3, BCl_3.
7. $X—Y_4$ (tetrahedral) Methane type	$\omega_i = 9$ $\nu(s)$; $\nu(a)$ (triple); $\delta(s)$ (double); $\delta(a)$ (triple)	CH_4, CCl_4, CBr_4, $SiCl_4$, $SnCl_4$, $TiCl_4$, $C(CH_3)_4$, $SnBr_4$.

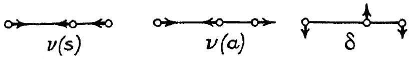
little to what molecular residue they are attached. Tables XIV and XV give just one or two examples of these " vibrations of radicals " and Table XVI a complete analysis of the methyl halides from this

point of view on the basis of the infra-red * and Raman data available.

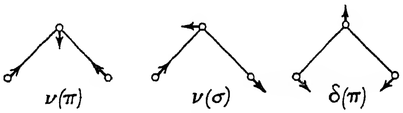
VI. These examples must suffice to show how quite simple molecular types, which, however, comprise a very large number of compounds, may be obtained by suitable combination of atoms into groups and by " splitting " and " bending " valencies. Of



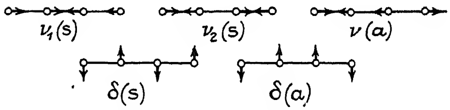
(1) Type X—Y, —C—H.



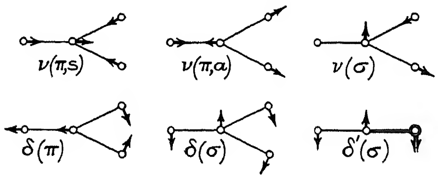
(2) Type Z—X—Y (straight), HCN.



(3) Type Y/X\Y (bent), H_2O.



(4) Type Y—X—X—Y (straight), C_2H_2.



(5) Type Z—X<(Y, Y) (plane), H_2CO.

Fig. 7.—Types of Vibration

course the complete solution of the proper frequency problem is not obtained in this way, but the frequencies thus obtained are the most important. In Table XVII (p. 47) I have summarized the most important cases; their vibration diagrams are given in figs. 7 and 8. The simple types 1–3 have already been discussed.

1. The " diatomic " molecule X—Y has *one* valency vibration,

* W. H. Bennett and C. F. Meyer, *Phys. Rev.*, **32**, 888 (1928).

and *two* deformation vibrations at right angles to it, which may possibly degenerate into a double vibration.

2. The linear molecule Z—X—Y (hydrocyanic acid type) has two valency vibrations; in one the *directions* of motion of the two outer atoms are mirror-image-like (symmetric), in the other anti-symmetric. As here we cannot speak of σ- and π-vibrations we call them (s) and (a);* (s) and (a), then, always refer to the nature of the vibrations of the *outer atoms*, whereas (π) and (σ) refer to those of the *central* atom. If the outer atoms are identical the symmetric frequency (infra-red-inactive, Raman-active) is the smaller of the two. The deformation vibration is always a degenerate double vibration, and is always infra-red-active.

TABLE XVIII

Proper Frequencies of the C_2H_n Molecule †

	$\nu_2(s)$	$\nu(a)$	$\nu_1(s)$	$\delta(a)$	$\delta(s)$
C_2H_2	3365	3276	1975	729	600
C_2H_4	3019	2990	1623	950	~800
C_2H_6	2950	2900	990	~1340	825

3. In the bent symmetrical Y—X—Y type of molecule (water type) all three proper frequencies $\nu(\pi)$, $\nu(\sigma)$, and $\delta(\pi)$ are infra-red-active and probably also Raman-active. The two valency frequencies become almost equal if the two valencies are at right angles or if there is a great disparity in mass ($X \ll Y$).‡

4. The next type, Y—X—X—Y (acetylene type) is extremely important and includes a large number of compounds. I shall confine myself to the data for the C_2H_n molecule (Table XVIII).§

* Here (s) and (a) refer only to the symmetry of the *direction* of vibration: symmetry of vibration in the ordinary sense, of course, only occurs in the symmetrical Y—X—Y molecule.

† In C_2H_4 the $—CH_2$ frequencies $\nu(\sigma, a) = 3107$, $\nu(\sigma, s) = 2880$, $\delta(\pi, s) = 1342$, and $\delta(\pi, a) = 1444$ also occur, corresponding to the vibration diagrams ν_4, ν_5, δ_4, and δ_3 in the paper cited.

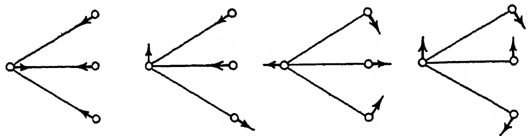
‡ The approximate formulæ (obtained by "splitting" the valency of X—(Y_2) and "bending" the linear Y—X—Y molecule) are as follows:

$$2\pi\nu_\pi = \sqrt{\frac{2k}{r^2}\left(\frac{1}{Y} + \frac{2\cos^2\alpha}{X}\right)} \quad \text{and} \quad 2\pi\nu_\sigma = \sqrt{\frac{2k}{r^2}\left(\frac{1}{Y} + \frac{2\sin^2\alpha}{X}\right)}.$$

§ The formulæ for the valency vibrations are given in R. Mecke, *Zeitschr. f. Physik*, 64, 173 (1930). I must expressly emphasize the fact that owing to some

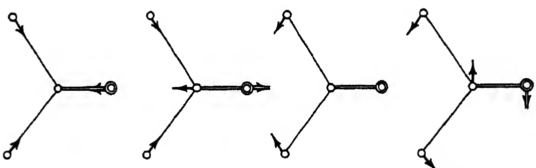
In particular, the benzene ring regarded as a C—(C_2)—(C_2)—C molecule falls under this heading. The two $\nu(s)$ vibrations are infra-red-inactive, Raman-active; similarly for $\delta(s)$. In the hydrocarbons ($Y \ll X$) $\nu_1(s)$ may be interpreted as a C—C vibration, $\nu_2(s)$ and $\nu(a)$ as C—H vibrations. The two deformation vibrations are degenerate double vibrations, so that only five proper frequencies are observed instead of the seven which one would expect.

5. The next type is the formaldehyde type (Z—X—Y_2). Here all the proper frequencies are active and none are degenerate (Table XIX), and may easily be calculated from types (2) and (3) by



$\nu(\pi)$ $\nu(\sigma)$ $\delta(\pi)$ $\delta(\sigma)$

(6) Type X<Y, Y, Y (pyramidal), NH_3



$\nu(s)$ $\nu(a)$ $\delta(s)$ $\delta(a)$

(7) Type Y, Y > X = Y_2 (tetrahedral), CH_4

Fig. 8.—Types of Vibration in XY_3 and XY_4

"splitting" and "bending" valencies. Degeneration occurs only in the plane XY_3 molecule (e.g. in the CO_3 group, according to Cl. Schaefer). Here $\nu(\pi, a) = \nu(\sigma)$ and $\delta(\pi) = \delta(\sigma)$; $\nu(\pi, s)$ is then infra-red-inactive.

In the three-dimensional molecules XY_3 and XY_4 (fig. 8) graphical representation becomes more difficult; we have taken the projection of the vibration in a plane through the axis of symmetry.

6. In the pyramidal model (ammonia type) we have two simple

recent investigations Table XVIII differs somewhat in certain respects from the statements made in that paper. In particular, some objections which were justly urged against my previous interpretation on account of symmetrical properties of the molecule thereby cease to apply.

vibrations $\nu(\pi)$ and $\delta(\pi)$ in which the Y_3 group vibrates as a whole, either with all the atoms moving in the direction of the valency bond ($\nu(\pi)$), or with all moving at right angles to this ($\delta(\pi)$). These vibrations may again be readily deduced from the type X—Y. In addition, two double vibrations occur, the three Y atoms oscillating in different ways in the two cases, in one in the directions of the valencies ($\nu(\sigma)$) and in the other at right angles to these ($\delta(\sigma)$), in such a way that the central atom always vibrates at right angles to the axis of symmetry. All four proper frequencies are active (Table XX).

TABLE XIX

Proper Frequencies of ZXY_2 Molecules

Y_2XZ	$\nu(\pi, s)$	$\nu(\sigma)$	$\nu(\pi, a)$	$\delta(\pi)$	$\delta(\sigma)$	$\delta(\sigma)$
H_2CO	2945		1770	1460	1040	920
Cl_2CO	571	444	1810	301?		
Cl_2SO	488	451	1229?	343?	282?	192?

TABLE XX

Proper Frequencies of XY_3 Molecules

XY_3	$\nu(\sigma)$	$\nu(\pi)$	$\delta(\pi)$	$\delta(\sigma)$
NH_3	3336		1630	933
PH_3	2327		1125	993
AsH_3	2127		906	1005
PCl_3	488	512	190	260
$AsCl_3$	370	410	159	193
$(HC)Cl_3$	761	666	259	366
$(HC)Br_3$	654	538	154	222

7. The tetrahedral molecule XY_4 (methane type) is best regarded as a Y_2—X—Y_2 molecule in which the two planes determined by $\genfrac{}{}{0pt}{}{Y}{Y}\!\!>\!X$ stand at right angles to one another. This model (Table XXI) has in the first place a simple symmetrical vibration $\nu(s)$, in which the outer atoms all move in the same way but the inner atom is at rest; i.e. the molecule pulsates and is therefore infra-red-inactive, Raman-active. It also has a triply degenerate asymmetrical vibration $\nu(a)$, which is active and in which the central atom moves on the surface of a sphere. Both frequencies may easily be calculated from

the symmetrical molecular type Y—X—Y. Finally, there also occur a triply degenerate deformation vibration $\delta(a)$, which is active, and a doubly degenerate deformation vibration $\delta(s)$, which is infra-red inactive. In view of the spherical symmetry of this type we

TABLE XXI

Proper Frequencies of Tetrahedral Molecules

XY_4	$\nu(a)$	$\nu(s)$	$\delta(a)$	$\delta(s)$
CH_4	3022	2915	1520	1304
CCl_4	792	459	313	214
CBr_4	667	265	183	123
$SnCl_4$	401	367	136	104
$SnBr_4$	279	220	88	64

cannot use the π, σ classification. The latter, however, can be applied to the molecular types Z—X—Y_3 (Table XVI) and Z_2—X—Y_2, where instead of four of the nine proper frequencies, six or nine different frequencies appear. These types have already been dealt with.

In addition to these seven molecular models there are of course others of interest; for example, the alcohol R—O—H type, corresponding to an unsymmetrical bent molecule, and the acid O=R—OH type are not included. Here the calculations become somewhat more involved. Chain compounds leading e.g. from the higher paraffins, sugars, albumens, and rubbers to crystals also promise interesting details for investigation. Ring compounds, too, require further examination. For example, the three-membered ring has three valency vibrations but *no* deformation vibrations. The four-membered ring has four valency vibrations and two deformation vibrations. The plane six-membered ring (benzene nucleus) is naturally of special interest. If there is hexagonal symmetry the twelve vibrations may be easily deduced to a first approximation from the linear C—C_2—C_2—C and the triatomic C_2—C_2—C_2, in which the binding constants must be suitably chosen by splitting the valencies. These simple examples should serve to demonstrate the " building-up principle * " sufficiently.

It may be advisable, however, to indicate the limits of applicability of the method sketched here, and thus to issue a warning against the exaggerated hopes with which I have frequently been confronted. It must always be borne in mind that here we are

* Ger. *Aufbauprinzip.*

dealing with an *approximate* method which is only intended to be accurate enough to enable us to establish the vibration diagram associated with an *observed* frequency. For this purpose it was necessary in the first place to investigate the binding forces in a diatomic or polyatomic molecule according to the experimental data available and then to develop a method of evaluation on the basis of simple mechanical ideas, by means of which the frequency might be estimated. It is out of the question, however, to evaluate the frequency spectrum corresponding to a given chemical structural formula in all its details, say in the way attempted by Andrews with his beautiful mechanical models of molecules, which will perhaps enable the calculation to be *simplified*. For such a calculation this method is not accurate enough, nor do we know the stresses controlling the configuration of the molecule with sufficient certainty —at least at present. In conclusion I should like to make this clear by means of a particularly glaring example, that of the tetrahedral model of carbon tetrachloride (CCl_4), in which four heavy outer atoms rich in electrons are attached to a light central atom. Here the symmetrical valency vibration readily gives the value 45V for the binding constant k by calculation from the simple formula $2\pi\nu_s = \sqrt{(2k/r^2Y)}$. As was shown by Table VIII (p. 39), this value is practically the same for all tetrachlorides, as in this symmetrical pulsation of the molecule the tetrahedral form is entirely preserved. If, however, we take the unsymmetrical vibration $\nu(a)$, which is associated with a considerable change of form, as was clearly exhibited even in the case of methane in the photographed band λ 8860, the appropriate formula $2\pi\nu_\sigma = \sqrt{\frac{2k}{r^2}\left(\frac{1}{Y} + \frac{4}{3X}\right)}$ gives a value of only 27V, which is almost the same as the value (31V) for the monochloride and corresponds without any doubt to a monovalent bond (see Tables V and VI, p. 38). We know from Debye's interferometric investigations, however, that a spreading of the angles of the tetrahedron occurs when the chlorine atoms are replaced by hydrogen. That is, when the symmetry is disturbed (as here by the vibration) the molecule readily tends to be deformed (see Table VII, p. 39). A similar but less marked case is that of carbon dioxide, $O{\equiv}C{\equiv}O$. The unsymmetric vibration $\nu(a)$ (2350), to be sure, gives a binding constant of 57V (see Table V, p. 38) which is nearly equal to the value characteristic of the divalent carbonyl bond ($=C=O$), but the symmetrical vibration $\nu(s)$ (1330),

which does not alter the form of the molecule, gives a higher value (67V), which, however, does not quite reach the value 77V for the triple bond. In both cases, then, we recognize definite indications of *rigidity of form* in the molecule (see Table II, p. 33), and it will be a task for the future to push the approximation further and thus to deduce the finer details of molecular structure from the observed frequencies.* For this it is absolutely essential that the frequency spectrum of the molecule should first be analysed and correctly interpreted as regards the character of the vibrations and of the bindings. The object of my remarks has been to point out a method which may lead to the desired goal.

If, however, we consider the difficulties which face us here and which I referred to above, we see how necessary it is that we should first obtain definite information on the various molecular data for the fundamental electronic state by combining investigations on the rotation-vibration bands in the infra-red and on the Raman spectra, at the same time making use of interferometric methods. With this as a foundation we may pass on to the study of different states of electronic excitation. In this field promising results have already been obtained. Hence when I look back from this point of view on the development of the spectrum analysis of diatomic molecules in the last eleven years, during which I have had the opportunity of working at the subject, I think I can safely say that in the near future we shall have advanced as far in the analysis of polyatomic molecules as we have to-day in that of diatomic molecules.

* See R. Mecke, *Zeitschr. f. phys. Chemie*, B, **16**, 409, 421 (1932); **17**, 1 (1932).

The Raman Effect and the Structure of Molecules and Crystals

F. RASETTI, ROME

This paper falls into two parts, one of a theoretical nature and the other partly of an experimental nature. The first part comprises the applications of the theory of the Raman effect to vibration (§§ 1, 2) and to rotation (§ 3). A special discussion of the CO_2 molecule is given in § 4. In the second part, after a brief account of the experimental technique for observing the Raman effect in crystals (§ 5), the phenomena observed in the case of rock salt are discussed in detail (§ 6).

§ 1. In the last year or two the Raman effect has become one of the most important means of investigating molecular structure. The theory of light-scattering in general enables definite statements about the structure of the body causing the scattering to be deduced from the scattered spectra observed experimentally. In the case of polyatomic molecules and still more in that of crystals, it is extremely difficult to solve the problem by a straightforward application of the general methods of quantum mechanics. Even for these systems, however, it is possible by making suitable assumptions to establish simple theorems relating to the scattering of light.

The theoretical discussion of the Raman effect is based on the Kramers-Heisenberg dispersion formula, in which the scattering moment of a system situated in the field of the incident light is expressed by the matrix elements of the electric dipole moment. A general consequence of the Kramers-Heisenberg formula is that in the passage from the state l to the state k in the Raman effect other states of the system also play an essential part, i.e. those which combine with the two states k and l (which in future we shall always refer to as "intermediate states"). The Smekal jump therefore

appears in the quantum theory as a double process; this is very clearly shown by the fact that in the limiting case, where the frequency of the incident light coincides with an absorption frequency of the system, the Raman effect passes into ordinary fluorescence. An important difference between fluorescence and the Raman effect is that in the former case only one intermediate state is involved in the process, whereas in the Raman effect there are in general an infinite number of intermediate states involved.

Most problems connected with the scattering of light by molecules and crystals, however, may be dealt with more easily by other methods which lead to the same results in simpler ways.

In what follows we shall chiefly be concerned with the vibrational Raman effect, i.e. with processes in which the vibrational quantum numbers alone vary. In such processes excited electronic states represent the essential intermediate states; this may easily be seen from the fact that light is also scattered by molecules in which vibration and rotation do not give rise to absorption or emission at all, such as non-polar diatomic molecules.

In these cases the summation for the excited electron terms which occurs in the Kramers-Heisenberg dispersion formula is very inconvenient, and in the particular case of polyatomic molecules, where little is known of the electronic states, almost impossible to carry out. If, however, as occurs in practice with the Raman effect, no one of the intermediate states plays a more important part than any other, i.e. the frequency of the incident light differs widely from the resonance frequencies of the molecule, it is not necessary to introduce the intermediate states explicitly. Instead, their joint effect may be taken account of by introducing the polarizability of the system as a function of the co-ordinates of vibration and rotation. In order to calculate the polarizability, it would of course be necessary to take the electron jumps into account; from a more empirical point of view, however, it may be regarded as given. As we shall see, some theorems with an important bearing on the Raman effect may be deduced in this way from a few quite simple general assumptions about the polarizability.

In treating the problem of scattering in this way we may apply the classical theory. The results obtained may easily be re-interpreted from the point of view of the quantum theory. It is also possible to start with the quantum theory and give an account of the phenomena which is closely related to the classical method.

As has been shown, e.g. by Tamm * for the problem of the scattering of light by crystals, this may be done very easily by means of Dirac's theory of radiation.

Without developing the theory in full we shall merely remark that the mutual action between the molecule and the radiation field which determines the scattering is represented by a term of the form

$$\frac{1}{2} \sum_{x,y,z} k_{xy}(\xi) E_x E_y \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in the Hamiltonian function, where the quantities $k_{xy}(\xi)$ represent the components of the tensor of the polarizability as functions of the co-ordinates (ξ) of the motion of the molecule (e.g. normal co-ordinates of the vibrations). The quantities E_x, E_y, E_z are the components of the electric field strength. In Dirac's theory the expression (1) is regarded as a perturbation term causing transitions between the quantum states of the undisturbed system (molecule + radiation field).

A simple calculation then shows that the Raman radiation corresponding to a transition of the system from state m to state n is determined by the matrix elements

$$\int \overline{\psi}_m(\xi) k_{xy}(\xi) \psi_n(\xi)\, d\xi. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

§ 2. We shall now consider the case of the vibrational Raman effect. Let ξ be the normal co-ordinate of a fundamental vibration of the molecule. To a first approximation we may regard the motion as harmonic, i.e. we may equate the $\psi_i(\xi)$'s to the Hermitian functions.

We shall develop the components of polarizability in powers of ξ in the form

$$k_{xy}(\xi) = k^0_{xy} + \alpha_{xy}\xi + \beta_{xy}\xi^2 + \ldots \quad . \quad . \quad . \quad . \quad (3)$$

The successive terms will decrease very rapidly in order of magnitude.

The constant term gives only diagonal elements, i.e. gives rise to Rayleigh scattering only. A Raman scattering in which the frequency is altered by a vibrational quantum will only be brought about if the quantities k_{xy} depend on ξ, because ξ possesses matrix elements for which $n = m \pm 1$. It follows that the Raman radiation in this case represents a process of higher order than the Rayleigh radiation. The overtones and the combination tones in the Raman effect similarly arise from the subsequent terms of higher order and the absence of harmonic character.

* I. Tamm, *Zeitschr. f. Physik*, **60**, 345 (1930).

In the Raman effect, then, only the fundamental vibrations will occur strongly. This was deduced by van Vleck * and Manneback † for diatomic molecules from the Kramers-Heisenberg formula in a rather more complicated way. From this formula, on the other hand, one would at first expect, in view of the Frank-Condon principle, that large jumps in the oscillation quantum number would be possible in the Raman effect. This apparent contradiction is cleared up by the fact that in the Kramers-Heisenberg dispersion formula the amplitudes of the terms arising from the various intermediate states are added and may thus partially cancel one another. In order to calculate the intensity of a vibrational Raman line we should have to sum for all the vibrational states of an excited electron term. From this summation it would appear that in the case of the overtones of the vibration frequency the disturbance due to interference is practically complete.

Bearing the same considerations in mind we can prove a further theorem. We suppose that the vibration is what we shall call an " even " one, i.e. the components of the polarizability are even functions of ξ. This may often be assumed without further investigation in view of the symmetry of the structure of the molecule. Then the quantities a_{xy} in the expression (1) are equal to zero; that is to say, to a first approximation the Raman radiation is absent.

These relationships have an important bearing on the interpretation of the vibrational Raman spectra. They show how the results obtained from investigations of the infra-red and of the Raman effect differ. In the infra-red there appear those frequencies which are active, i.e. which are associated with a dipole moment varying with time; in the Raman effect, on the contrary, there appear only those frequencies which are not even. Overtones and combination tones are exhibited only very feebly in the Raman effect.

§ 3. We now turn to rotational Raman spectra. These have chiefly been investigated for diatomic molecules,‡ and the selection rules may be deduced very easily from the Kramers-Heisenberg formula.

In the molecules which have actually been investigated the fundamental state is a $^1\Sigma$ state (in oxygen it is a $^3\Sigma$ state, but the triplet structure has no effect on the Raman spectrum), that is,

* J. H. van Vleck, *Proc. Nat. Acad. Amer.*, **15**, 754 (1929).

† C. Manneback, *Zeitschr. f. Physik*, **62**, 224 (1930).

‡ R. W. Wood, *Phil. Mag.*, **7**, 744 (1929); F. Rasetti, *Proc. Nat. Acad. Amer.*, **12**, 284, 515 (1929); *Phys. Rev.*, **34**, 467 (1929); *Zeitschr. f. Physik*, **61**, 598 (1930).

to a first approximation the molecule has the properties of a simple rotator. The energy of rotation is given by

$$E(J) = BhJ(J+1).$$

As is well known, the terms of a diatomic molecule are classified by Kronig into two classes, even terms and odd terms, with the property that the even terms will only combine with the odd terms and vice versa. In a definite Σ electron state the rotation terms are alternately even and odd. From the Kramers-Heisenberg formula it then follows at once that in the Raman effect only transitions between terms of the same class can take place. For the Raman effect the ordinary rule of selection $\Delta J = 0, \pm 1$ leaves of these transitions only those for which $\Delta J = 0, \pm 2$.

The rotation spectrum will therefore consist of lines for which the Raman shift is

$$\frac{1}{h}\Big(E(J+2) - E(J)\Big) = B(4J+6).$$

The interval between successive lines will be $4B$, but the interval between the first Raman line and the exciting line is $6B$.

These relationships are exhibited very clearly, e.g. by hydrogen. Owing to the smallness of the moment of inertia ($B = 60$ cm.$^{-1}$) only very few rotation lines occur here. Heavier molecules are at ordinary temperatures distributed among a large number of rotation states, and accordingly many Raman lines appear (O_2, $B = 1{\cdot}43$; N_2, $B = 1{\cdot}99$). The intensity distribution is similar to that in the ordinary bands; for details see Manneback * and Segrè.†

In the case where the molecule consists of two identical atoms, further special consequences of the quantum-mechanical resonance between the two nuclei must be borne in mind. The alternating intensities of the rotation lines resulting from these relationships are, as is well known, of importance in determining the statistics and spin of the atomic nuclei. In the case of nitrogen the anomalous statistics of the nuclei and the value of the moment of inertia were first obtained from the Raman effect.‡

Of course a rotational structure must also be present in vibrational Raman lines. In Σ electron terms we may expect the three branches Q, RR, and PP. A band like this has in fact been observed in the

* C. Manneback, *Zeitschr. f. Physik*, **62**, 224 (1930).

† E. Segrè, *Rend. Linc.*, **11**, 825 (1930).

‡ W. Heitler and G. Herzberg, *Naturwiss.*, **17**, 673 (1929); F. Rasetti, loc. cit.

case of hydrogen and is shown in Plate III, fig. 1. As a rule, however, the Q-branch is alone observed, because its lines practically coincide and even singly possess a higher intensity than those of the other branches.*

Finally, the electronic state may also vary in the Raman effect. It is only in one case where the fundamental term is multiple (the $^2\Pi$ term of nitric oxide) that it has been possible to detect a transition between the two components of the doublet.†

§ 4. We shall now give a detailed account of the relationships between the structure of a polyatomic molecule and its Raman spectrum in a particular case, and for this purpose we select the important one of the CO_2 molecule.

The model of this molecule is assumed to be linear. The fundamental vibrations have been discussed in detail by Dennison and

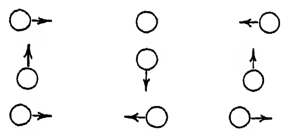


Fig. 5

others. They are sufficiently illustrated by fig. 5. The frequency ν_1 is optically inactive, that is, only ν_2 and ν_3 will be observed in the infra-red. In the Raman effect, on the other hand, only the odd frequency ν_1 will appear.

The active frequencies ν_2 and ν_3 are to be identified with the bands which appear strongly at 675 and 2350 cm.$^{-1}$ in the infra-red.‡ If we assume that the oxygen atoms are attached to the carbon atom only and exercise no force on each other, we find that we must have $\nu_3 \cong 1{\cdot}91\nu_1$. That is, the inactive frequency should lie at about 1230 cm. In actual fact, however, we find two Raman lines § near this but with a wave-number about 100 units higher. The occurrence of this structure instead of a single line is at first sight very surprising, and it has only recently been explained by Fermi.|| In view of this explanation the classification of the fre-

* C. Manneback, loc. cit.

† F. Rasetti, *Zeitschr. f. Physik*, **66**, 646 (1930).

‡ Barker, *Astrophys. Journ.*, **55**, 391 (1922); Eucken, *Zeitschr. f. Physik*, **37**, [illegible] 1926).

§ F. Rasetti, *Nature*, **123**, 205 (1929); Dickinson, Dillon, and Rasetti, *Phys. Rev.*, **34**, 582 (1929).

|| E. Fermi, *Zeitschr. f. Physik*, **71**, 250 (1931).

quencies of the CO_2 molecule given above may probably be regarded as satisfactory.

According to Fermi the cause of the splitting-up lies in the accidental quasi-coincidence of the states in which a vibrational quantum of frequency ν_1 or two quanta of frequency ν_2 are excited. From resonance between these two states there arise two energy levels differing fairly widely from one another, if we assume that there is mutual action between the two vibrations. The proper functions corresponding to the perturbed proper values are linear combinations of the proper functions of the vibrations ν_1 and ν_2, and contain about fifty per cent of the proper function of ν_1. Owing to the occurrence of the proper function of ν_1, which is active in the Raman effect, these terms both combine with the fundamental term and give the two strong Raman lines observed at 1284 and 1387 cm.$^{-1}$. Their separation was also calculated by Fermi, the result being in good agreement with experiment. Two feeble lines also appear in the Raman spectrum; these have been identified very satisfactorily as arising from a thermally-excited energy level of 675 cm.$^{-1}$.

The same explanation as in the case of CO_2 seems to hold also in other cases where more Raman lines are found than can be accounted for by the ordinary theory. Thus for example in CS_2, which is analogous to CO_2, we again have a Raman doublet, although in this case the unequal intensity of the two components shows that the relation $\nu_1 = 2\nu_2$ is only very roughly satisfied. Another very well known case is that of CCl_4, where the Raman doublet $\nu = 758$, 789 cm.$^{-1}$ can be explained, according to Fermi, by the existence of a relationship of the type $\nu_1 + \nu_2 = \nu_3$.

§ 5. I should now like to describe some new observations on the Raman spectra of crystals.

The arrangement of the experiments was essentially that used for gases. The source of light consists of a Heraeus mercury lamp cooled by running water. This lamp emits an extremely sharp and intense resonance line λ 2537, which was alone used for exciting the Raman spectra. This type of excitation has three main advantages. In the first place, the Raman lines are excited very strongly, owing to the great intensity of the primary line and the rapid increase of scattering with frequency. In the second place, greater frequency shifts are obtainable than with excitation by visible light. In the third place, after the Raman lines have been excited the primary line may readily be absorbed by mercury vapour, which enables observations to be made of extremely small frequency shifts.

The Raman spectra produced by this method are extremely intense. For example, the strongest Raman line of calcite was shown on the plates with an exposure of only a minute. The very disturbing fluorescence which occurs when visible light is used is entirely absent in the ultra-violet.

In all the crystals investigated new feeble Raman lines were observed, especially those with a small frequency shift (sometimes as low as 40 cm.$^{-1}$). Raman spectra were also observed in crystals which had previously been investigated without success, namely, in rock-salt and fluorite. The Raman effect in NaCl will be discussed below in detail.

In fluorite and calcite, besides the ordinary Raman lines, some lines were found at about λ 3100, which in a preliminary communication * were interpreted as being Raman lines with a very large frequency shift (of the order of 7000 cm.$^{-1}$), excited by the mercury line λ 2537. Professor Tomaschek † pointed out that in the case of CaF_2 the wave-lengths of these lines coincide very closely with those of the known fluorescence lines of gadolinium, and proposed to explain the lines observed by me in this way. The agreement is so exact that I consider it extremely probable that this explanation is the correct one. Although the samples of crystals used were absolutely colourless, it is not difficult to admit that rare-earth impurities may have been present in an amount which, though extremely small, was sufficient to bring out fluorescence lines under the special conditions of strong illumination and long exposure in these experiments. The spectrum of gadolinium in $CaCO_3$ has not been investigated, but from the similarity of the fluorescence spectrum to that observed with CaF_2 it is reasonable to assume that the lines belong to the same element.

Fig. 2 of Plate III shows the spectrum of $CaCO_3$ excited by the mercury line λ 2537, photographed with a large Hilger E1 spectrograph. Fig. 3 shows the characteristic group of the four gadolinium lines on a larger scale.

§ 6. We shall now turn to the Raman effect in rock-salt. The Raman spectrum of NaCl differs from those usually observed in the case of crystals not only as regards its feebleness (eight hours' exposure with particularly intense irradiation was required to give the Raman effect), but also as regards its structure. Whereas the Raman spectrum of all other crystals which have been investigated

* F. Rasetti, *Nature*, **127**, 626 (1931).

† R. Tomaschek, *Nature*, **128**, 495 (1931).

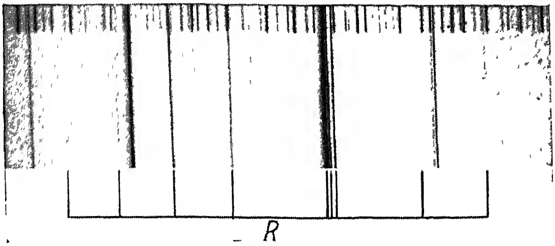


Fig. 1

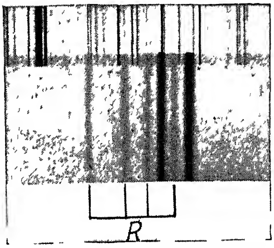


Fig. 3

Fig 2

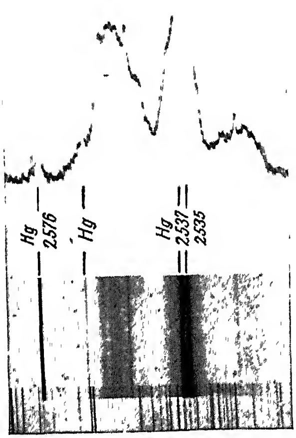


Fig 4

consists of more or less sharp lines, in the case of rock-salt it is continuous. It extends from the neighbourhood of the exciting line to a distance of about 365 cm.$^{-1}$ and possesses various maxima and minima of intensity. At 365 cm.$^{-1}$ the intensity suddenly falls. The anti-Stokes spectrum is also well marked. This Raman spectrum is reproduced in Plate III, fig. 4. The intensity distribution is best seen from the photometer curve.

An explanation of this behaviour which is at least qualitative has been given by Fermi.* We cannot go into the details of the theory here, but will merely indicate its general features.

As is well known, a crystal lattice consisting of n elementary lattices in general possesses $3n$ proper frequencies for each (vectorial) wave-number. As the wave-number vanishes three of these frequencies associate themselves with the acoustic vibrations (zero frequency) and the other $3n - 3$ with infra-red frequencies. Now it may be shown that to a first approximation only those frequencies with vanishing wave-number (or, more accurately, with an elastic wave-number of the order of magnitude of the optical wave-number) are effective in the Raman effect. It follows that crystals ordinarily give sharp Raman lines corresponding to the proper vibrations with vanishing wave-number, i.e. to the vibrations of the various elementary lattices relative to one another.

In order to see this more clearly we consider an element of a crystal, with linear dimensions small compared with the wave-length of the incident light, but still containing a large number of atoms. Under these conditions the scattering will depend on the induced electric moment. This is proportional to the polarizability.

The occurrence of Raman scattering is therefore due to the fact that the elastic proper vibrations of the crystal lattice produce changes in the polarizability, which give rise to combination frequencies in the electric moment. To a first approximation we may assume that the change in the polarizability is proportional to the elastic stress. It then turns out that only those proper vibrations are effective in the Raman effect for which the whole crystal vibrates in the same phase, i.e. those for which the wave-number vanishes. If, on the other hand, the crystal under consideration contains many elastic wave-lengths, the mean variation of the polarizability vanishes to a first approximation.

Experiment entirely confirms these ideas. Raman lines corresponding to the vibrations of the elementary lattices relative to one

* E. Fermi and F. Rasetti, *Zeitschr. f. Physik*, **71**, 689 (1931).

another have been observed in a large number of crystals. In the case of crystals also it is to be noted that even vibrations are inactive in the Raman effect. For example, only one of the two proper frequencies of fluorite appears in the Raman effect; it corresponds to a vibration of the two F lattices relative to one another, the Ca lattice remaining fixed. It may be shown that this vibration is the only one which is not even.*

The proper frequencies of the CO_3 group form another striking example. This group has four different fundamental frequencies, of which one is even, i.e. is inactive in the Raman effect, the others being odd and occurring in the Raman effect for all substances containing the CO_3 group. In calcite, for example, they lie at 714, 1085, and 1435 cm.$^{-1}$, whereas the frequency which is inactive in the Raman effect is observed in the infra-red at 880 cm.$^{-1}$.

In the rock-salt lattice the *one* infra-red proper vibration is even. To a first approximation, therefore, a Raman spectrum does not occur in this case. Raman scattering then arises only from the quadratic and higher order terms in the relationship between the polarizability and the elastic stress, i.e. has a much smaller intensity. Then, however, the proper vibrations with arbitrary wave-numbers also come under consideration, because in the averaging over the different phases of the elastic motion in space the quadratic terms do not vanish. If, however, all the proper vibrations contribute towards altering the polarizability, a continuous Raman spectrum will be observed. In fact closer consideration shows that in the Raman effect there occur all the possible sums and differences of the frequencies associated with each wave-number. The highest frequency in the Raman effect will accordingly be equal to twice the proper frequency with wave-number zero. In actual fact the maximum frequency in the Raman spectrum of NaCl is about 365 cm.$^{-1}$, which is in sufficient agreement with double the infra-red proper frequency.

* F. Rasetti, *Nature*, **127**, 626 (1931); E. Fermi and F. Rasetti, *Zeitschr. f. Physik*, **71**, 689 (1931).

The Raman Effect and Molecular Structure

G. PLACZEK, Leipzig

§ 1. The Raman Effect as a result of Interaction between the Nuclear and Electronic Motions

In what follows we shall give a brief survey of the newer methods which have been used in the investigation of molecular structure by means of the Raman effect. For this purpose we must first make the general laws of this effect clear. This may be done in two ways. In the first,* we start from the dispersion formula given by quantum mechanics,† which is a *perfectly general* description of the properties of the scattered radiation of an arbitrary system, and in evaluating it by successive transformations and summations we take account of the *special* relationships which occur in the case of molecules irradiated by visible and ultra-violet light. This method is fairly troublesome and can be successfully applied in the case of diatomic molecules only, as the knowledge of the properties of the excited electronic states necessary for carrying out the process is not available for polyvalent molecules. The second method ‡ consists in first investigating the special physical character of the problem (as compared with the general dispersion theory) and then immediately proceeding to select a method suited to it. This is done as follows.

As is well known, the scattering of light under ordinary conditions is practically due to the *electrons* alone, owing to the great mass of the nucleus; the frequency changes connected with the scattering,

* A. Carelli, *Rend. Linc.* (6), 8, 155 (1928); E. L. Hill and E. C. Kemble, *Proc. Nat. Acad. Amer.*, **15**, 387 (1929); J. H. van Vleck, *Proc. Nat. Acad. Amer.*, **15**, 754 (1929); G. Placzek, *Zeitschr. f. Physik*, **58**, 585 (1929); C. Manneback, *Zeitschr. f. Physik*, **62**, 224 (1930).

† H. A. Kramers and W. Heisenberg, *Zeitschr. f. Physik*, **31**, 681 (1925); P. A. M. Dirac, *Proc. Roy. Soc.*, A, **114**, 710 (1927).

‡ G. Placzek, *Zeitschr. f. Physik*, **70**, 84 (1931).

however, give rise to a transference of energy to the *nuclei*.* In order that this transference may take place, it is necessary that the motions of the electrons and of the nucleus should be coupled. The possibility of the Raman effect occurring therefore depends on this; the theory of the Raman effect will be obtained by investigating how the scattering is affected by the interaction of the motions of the nucleus and of the electrons. This may be done either formally by a simple perturbation calculation or by a physical method. Here we choose the latter alternative, and begin by considering the scattering of a molecule whose nuclei are held fast in any position, the latter being determined by the moment induced by an external field of frequency ν,

$$M = \alpha E.$$

In general the polarizability α also depends on the direction of the field relative to the molecule; it is a symmetric tensor and may, as we know, be represented by an ellipsoid whose axes are fixed in the molecule. For the separate components of this tensor the dispersion theory gives the expression

$$\alpha_{xy} = \frac{1}{h} \sum_e \frac{\nu_e Y_{0e} X_{0e}}{\nu_e^2 - \nu^2}, \qquad \qquad (1)$$

where the ν_e's are the absorption frequencies of the (electronic) fundamental state, and X_{0e}, Y_{0e} the electric moments, in the x and y directions respectively, associated with the spontaneous transitions of the excited states to the fundamental state. (Here and in what follows, where not otherwise stated, α_{xy} stands for any of the components of α.) The difference between (1) and the (much more complicated) expression for a moving molecule consists in the fact that in the latter the summation has also to be extended over the vibrational and rotational states.

We have now to investigate the interaction between the motions of the nucleus and of the electrons. This manifests itself as follows.

1. The position of the electron terms of a molecule with fixed nuclei depends on the *internuclear distances*, as is shown in detail in Hund's correlation theory;† hence in the motion of the nuclei there will be a periodic shift of the electron terms; the same is true for the probabilities of transition, X_{0e}, Y_{0e}.

2. If the nuclei are moving, each individual electron term will

* Here we may overlook the possible occurrence of electron jumps in the Raman effect, as only a single case has been substantiated hitherto.

† F. Hund, *Phys. Zeitschr.*, 31, 876 (1930).

split up into a series of vibration terms and rotation terms. The extent of the separation is determined by the frequency of the nuclear motion, i.e. the *nuclear velocities*.

For our problem we are only interested in the integral effect of these considerations in modifying equation (1). Here it is to be noted that the changes caused by the nuclear velocities can only affect α if the interval $\nu_e - \nu$ is comparable with the extent of the separation of the electron terms, which is of the order of magnitude of the nuclear frequency ν_k. If the incident frequency is so chosen that this is not the case, we can sum up the whole effect of the nuclear motion on the scattering by regarding α as dependent on the co-ordinates of the nucleus only, i.e. under these conditions the scattering of a vibrating and rotating molecule is the same for every instantaneous position of its nuclei as that of a molecule with nuclei held fast in that position.

Now if we are concerned not with the scattering for a definite position of the nuclei, but with the scattering for a definite quantum state (of vibration and rotation) r, we have to average over all positions which are possible in that state. As the probability that a nucleus shall occupy a certain position is given by the quantity $\psi_r\psi_r^*$, where ψ_r is the nuclear proper function of the *fundamental* electronic state, the scattering is given by

$$(M_{xy})_{rr} = E\int \alpha_{xy}(q)\psi_r(q)\psi_r^*(q)\,dq, \quad . \quad . \quad . \quad (2a)$$

where q stands for all the co-ordinates of the nucleus; similarly, we obtain for the scattering associated with the transition between two nuclear states r, r' (Raman effect)

$$(M_{xy})_{rr'} = E_y\int \alpha_{xy}(q)\psi_r(q)\psi_{r'}^*(q)\,dq. \quad . \quad . \quad (2b)$$

(The variation with time is obtained by integration over the imaginary parts of the proper functions ψ_r, which, as we know, have the form $e^{2\pi i(E_r t + \phi_r)/h}$. After combination with $e^{2\pi i\nu t}$, the time factor of the incident wave, this leads to the time factors $e^{2\pi i\nu t}$ for (2*a*) and $e^{2\pi i(\nu + \nu_{rr'})t + \phi_{rr'}}$ for (2*b*), as it ought.) In (2*a*) and (2*b*) we have accordingly obtained expressions which are easy to evaluate, as they now contain quantities relating to the *fundamental* electronic state. The effect of the excited states is already contained implicitly in the polarizability and its relationship to the nuclear co-ordinates. As we shall show in what follows, moreover, to deduce the most important intensity rules and all the polarization and selection rules we do not need to know anything about this relationship whatever.

§ 2. Intensity and Polarization

To evaluate the integrals we consider the proper function of the nuclear motion of a molecule (ψ_r). If we at first neglect the interaction of vibration and rotation,* this proper function may be expressed as the product of the proper function of the rotation and the proper function of the vibration. The former depends on the Eulerian angles, the latter on the normal co-ordinates of the vibrations. To begin with we integrate over the proper function of the vibration alone, which may be done by considering the scattering not in a system of co-ordinates fixed in space but in a system of co-ordinates fixed in the molecule; then the whole nuclear proper function is represented by the proper function of the vibration. We put $\alpha_{xy} = (\alpha_{xy})_0 + \Delta\alpha_{xy}$ (where $(\alpha_{xy})_0$ is the component of polarizability in the position of equilibrium); then, bearing in mind that

$$\int \psi_v \psi_{v'}^* \, dq = \delta_{vv'}$$

we put

$$\left.\begin{aligned} (M_{xy})_{vv} &= E_y \int \{(\alpha'_{xy})_0 + \Delta\alpha'_{xy}\} \psi_v \psi_v^* \, dq \\ &= E_y \int \{(\alpha'_{xy})_0 + (\Delta\alpha'_{xy})_{vv}\}, \\ (M_{xy})_{vv'} &= E_y (\Delta\alpha'_{xy})_{vv'} \end{aligned}\right\} \quad . \quad . \quad (3)$$

for the scattering. (The dash on the quantities α indicates that they refer to the system of axes fixed in the molecule; v, v' denote the totality of the vibrational quantum numbers.)

The integration (formation of the matrix element) means that from the whole distortion $\Delta\alpha$ of the polarizability that part is selected which has the time factor $e^{2\pi i \nu_{vv'} t}$ and when multiplied by the incident wave accordingly gives a scattered radiation of frequency $\nu + \nu_{vv'}$. Like α, the quantity $(\Delta\alpha)_{vv'}$ is a symmetric tensor and may also be represented by an ellipsoid.

The passage from the system of co-ordinates fixed in the molecule to the system of co-ordinates fixed in space represented by integration over the rotational proper functions may (as is shown in the paper cited in the third footnote on p. 65) be made by taking the classical average of the scattered intensity over all orientations of the tensor ellipsoid $(\Delta\alpha)_{vv'}$ relative to the axes fixed in space, seeing that in most

* This is taken account of in § 3.

molecules the rotational levels are sufficiently excited even at room temperatures. We thus obtain the sum of the intensities of *all* transitions (with or without a change in the rotational quantum numbers) which are associated with a jump in the vibrational quantum number. It is this very quantity, however, that is experimentally of importance, as it is only all these transitions acting together that give a Raman line. The resolution of a Raman line into the pure vibration line (Q-branch) and the various rotation lines is possible only in molecules with a very small moment of inertia and hitherto has only been realized in H_2 and CH_4.*

The averaging over the intensity is identical with the solution of the problem of forming the average of the squares and doubled products of tensor components c_{ik} taken for all orientations of the tensor ellipsoid. If the quantities c_j denote the three principal values of the tensor ellipsoid,

$$A = \sum_j c_j$$

their sum, and

$$j = \tfrac{1}{4}\sum_j (c_j - c_k)^2$$

the anisotropy of the tensor, an easy calculation gives

$$\left.\begin{aligned}
\overline{c_{ii}^2} &= \overline{(\textstyle\sum_j \alpha_j \cos^2 ij)^2} = \tfrac{1}{45}(5A^2 + 4\gamma^2).\\
\overline{c_{ik}^2} &= \overline{(\textstyle\sum_j \alpha_j \cos ij \cos kj)^2} = \tfrac{1}{15}\gamma^2\\
\overline{c_{ii}c_{kk}} &= \overline{\textstyle\sum_j \alpha_j \cos^2 ij \sum_j \alpha_i \cos kj} = \tfrac{1}{45}(5A^2 - 3\gamma^2)\\
\overline{c_{ik}c_{kl}} &= \overline{(\textstyle\sum_j \alpha_i \cos ij \cos kj)(\sum_j \alpha_i \cos kj \cos lj)} = 0.
\end{aligned}\right\} \quad . \qquad (4)$$

The tensor $(\Delta\alpha)_{vv'}$ determines the intensity and polarization of the Raman lines for any composition of the incident light. If the latter is polarized, we have

$$\left.\begin{aligned}
\overline{|(M_x)_{vv'}|^2} &= \overline{|(\alpha_{xx})_{vv'}|^2}E^2 = \frac{E^2}{45}(5A^2_{vv'} + 4\gamma^2_{vv'})\\
\overline{|(M_y)_{vv'}|^2} &= \overline{|(\alpha_{xy})_{vv'}|^2}E^2 = \frac{E^2}{45}\cdot 3\gamma^2_{vv'}\\
\overline{|(M_z)_{vv'}|^2} &= \overline{|(M_y)_{vv'}|^2}
\end{aligned}\right\} \qquad (5)$$

the x-axis of the system of co-ordinates fixed in space being taken in

* F. Rasetti, *Phys. Rev.*, **34**, 367 (1929) (H_2); Dickinson, Dillon, and Rasetti, *Phys. Rev.*, **34**, 582 (1929) (CH_4).

the direction of the electric vector of the incident wave. The depolarization is given by

$$\rho = \frac{\overline{|(M_y)_{vv'}|^2}}{\overline{|(M_x)_{vv'}|^2}} = \frac{3\gamma_{vv'}^2}{5A_{vv'}^2 + 4\gamma_{vv'}^2}. \quad . \quad . \quad . \quad (6)$$

In the case of ordinary incident light we may easily verify the truth of the well-known relationship

$$\rho_n = \frac{2\rho}{1+\rho}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6a)$$

As (6) shows, the depolarization ρ varies between $0\,(\gamma_{vv'} = 0$, spherical tensor) and $\frac{3}{4}\,(A_{vv'} = 0)$. For ordinary light (6*a*) the latter value becomes $\frac{6}{7}$. In the case of the undisplaced line, whose polarization is determined by the tensor α itself, it is to be noted that A is always greater than γ, as the principal values of α must always be positive. Hence in this case the upper limit of the depolarization is $\frac{1}{3}$. In the case of the tensors $(\Delta\alpha)_{vv'}$, on which the Raman effect depends, this is no longer true, as the polarizability may increase or decrease during the vibration. Hence if in this case ρ is greater than $\frac{1}{3}\,(\rho_n > \frac{1}{2})$, it always means that the polarizability increases in some directions and decreases in others. (The converse, however, is not true.) For a series of vibrations including all the degenerate ones we have, as is shown in § 3 (p. 71), $A_{vv'} = 0$ for reasons of symmetry; for these, therefore, $\rho = \frac{3}{4}\,(\rho_n = \frac{6}{7})$. This fact is frequently of importance in the classification of lines.

Hanle * and Bär † have recently embarked on polarization experiments in which circularly polarized light is used. They find that in a number of lines the sign of the circular polarization of the light scattered in the direction of propagation is changed (with right-handed circular polarization of the incident light the polarization of the scattered light is left-handed), whereas with other lines this is not the case. As is clear from the foregoing, these facts must be quantitatively dealt with by the above methods; the averaging over the orientations of the ellipsoid has merely to be adapted to the case of circularly polarized incident radiation.

If we put

$$\begin{aligned} E_x &= E\cos 2\pi\nu t \\ E_y &= E\sin 2\pi\nu t \\ E_x + iE_y &= Ee^{2\pi i\nu t} \end{aligned}$$

* W. Hanle, *Naturwiss.*, **19**, 375 (1931); *Phys. Zeitschr.*, **32**, 556 (1931).

† R. Bär, *Naturwiss.*, **19**, 463 (1931); *Helv. Phys. Acta*, **4**, 131 (1931).

the scattering is

$$(M_x + iM_y)_{vv'} = (\alpha_{xx} + i\alpha_{yx})_{vv'} E_x + (\alpha_{xy} + i\alpha_{yy})_{vv'} E_y$$
$$= E\left\{\left(\frac{\alpha_{xx} + \alpha_{yy}}{2}\right)_{vv'} e^{2\pi i\nu t} + \left(\frac{\alpha_{xx} - \alpha_{yy} + 2i\alpha_{xy}}{2}\right)_{vv'} e^{-2\pi i\nu t}\right\}. \quad (7)$$

Equation (7) represents the decomposition of elliptically polarized scattered radiation into two parts which are circularly polarized in opposite senses, the first being in the same sense as the incident light, the second in the opposite sense. The ratio of the intensities of these two components is then determined experimentally (by separating them with a quarter-wave plate).

Equation (4) gives the following expressions for the intensities:

$$\left.\begin{aligned}\overline{|(M_c)_{vv'}|^2} &= \overline{\left|\left(\frac{\alpha_{xx} + \alpha_{yy}}{2}\right)_{vv'}\right|^2} . E^2 = \frac{E^2}{45}(5A^2_{vv'} + \gamma^2_{vv'}) \\ \overline{|(M_r)_{vv'}|^2} &= \overline{\left|\left(\frac{\alpha_{xx} - \alpha_{yy} + 2i\alpha_{xy}}{2}\right)_{vv'}\right|^2} E^2 = \frac{E^2}{15} . 2\gamma^2_{vv'}\end{aligned}\right\} \quad (8)$$

and the ratio of the "reversely" and "correctly" circularly polarized intensities is

$$\frac{I_r}{I_c} = \frac{\overline{|(M_r)_{vv'}|^2}}{\overline{|(M_c)_{vv'}|^2}} = \frac{6\gamma^2_{vv'}}{5A^2_{vv'} + \gamma^2_{vv'}}. \quad . \quad . \quad . \quad (9)$$

From (9) and (6) it follows that

$$\frac{I_r}{I_c} = \frac{2\rho}{1 - \rho}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (6b)$$

As (6*b*) shows, the scattered radiation is "correctly" polarized for $\rho < \frac{1}{3}$, unpolarized for $\rho = \frac{1}{3}$, and "reversely" polarized for $\rho > \frac{1}{3}$. For $\rho = \frac{3}{4}$ the ratio $I_r/I_c = 6$. A discussion of the conditions under which the various cases occur has been given above.

Like the results of polarization experiments with linearly polarized or ordinary incident radiation, the results of experiments with circularly polarized incident radiation may be applied to the classification of lines.

§ 3. The Selection Rules

Selection rules in general result from properties of symmetry in the system under consideration. In order to deduce them in

the case of the Raman effect we have accordingly to investigate the effect of molecular symmetry on the quantities *

$$(\alpha_{ik})'_{vv'} = \int \alpha'_{ik}(q)\psi_v(q)\psi_{v'}{}^*(q)\,dq.$$

We first regard the vibrations of the molecules as harmonic; then the proper functions ψ_v are products of proper functions of the harmonic oscillator (the well-known Hermite polynomials†), each of which depends on only one normal co-ordinate:

$$\psi_v = \psi_{v1}\psi_{v2} \ldots \psi_{vj} \ldots \psi_{v3n-6}.$$

The functions ψ_{vj} are even or odd functions of their argument according as the quantum number v_j is even or odd. If we first confine ourselves to those transitions in which only *one* of the quantum numbers v_j is altered, the product $\psi_{v_j}\psi_{v'_j}$, and hence also the whole product $\psi_v\psi_{v'}{}^*$, is an even or odd function of q_j, according as Δv_j is even or odd. As we have to integrate with respect to q_j from $-\infty$ to $+\infty$, $(\alpha_{ik})_{vv'}$ vanishes if the integrand is an odd function of q_j. This is the case for

$$\left.\begin{aligned} \Delta v_j &= 0, 2, 4, \ldots \text{ if } \alpha_{ik}(q_j) = -\alpha_{ik}(-q_j) \\ \Delta v_j &= 1, 3, 5, \ldots \text{ if } \alpha_{ik}(q_j) = \alpha_{ik}(-q_j). \end{aligned}\right\} \quad . \quad (10)$$

The vanishing of a component of the tensor α may give rise to a definite polarization of the scattered radiation. If *all* the components of α are even or odd functions of q_j, the corresponding line is "forbidden" in the Raman effect.

These rules, moreover, may easily be adapted for cases in which several vibrational quantum numbers are changed simultaneously (combination tones). In order that the integral may vanish here, it is sufficient that (10) should be satisfied for any one of the normal co-ordinates involved in the combination tone. (The simple combination tone, for example, vanishes when one or both of the conditions $\alpha(q_j) = \alpha(-q_j)$; $\alpha(q_l) = \alpha(-q_l)$ hold good.)

To obtain the selection rules we have now to ascertain when conditions of the type (10) hold good. This leads to a general investigation of the symmetrical properties of proper vibrations.

* In this section the tensor components are always those relative to the system of co-ordinates fixed in the molecule. The dash on the α hitherto used to indicate this will in future be omitted.

† Cf. e.g. Sommerfeld, *Wave-Mechanics* (Methuen, 1930).

We consider the potential energy of a vibrating molecule:

$$V = \tfrac{1}{2}\sum_j \lambda_j q_j^2. \qquad (\lambda_j = 4\pi^2\nu_j^2)$$

V must be invariant with respect to all symmetrical operations permitted by the symmetry of the (undistorted) molecule. This is attainable if:

(*a*) q_j is replaced by q_j or $-q_j$ as the result of a symmetrical operation; the proper vibrations are either symmetrical or antisymmetrical with respect to the element of symmetry under consideration; or

(*b*) q_j is replaced by a linear combination of normal co-ordinates:

$$q_j \rightarrow L(q_j, q_k, q_l).$$

In order that V may remain invariant in such a case, it is necessary that

$$\lambda_j = \lambda_k = \lambda_l;$$

that is, the frequencies are equal and the vibration is degenerate; we say that its symmetry is degenerate with respect to the element of symmetry. The symmetry of any proper vibration is accordingly classified by describing its character (symmetrical, antisymmetrical, degenerate) relative to all the elements of symmetry of the molecule.

If we begin by considering vibrations which are antisymmetrical with respect to any one of the elements of symmetry which occur, the conditions (10), and hence the selection rules, are always fulfilled if α_{ik} remains unaltered (for odd Δv_j) or its sign alters (for even Δv_j) as a result of the symmetrical operation. We have now to investigate how the tensor α or its components α_{ik} behave relative to symmetrical operations. As tensor components transform in the same way as the products of the co-ordinates, we have merely to consider the behaviour of the latter.

We shall illustrate this by the simplest possible example, that of the plane of symmetry. If we take this as xy-plane,

$$x \rightarrow x$$
$$y \rightarrow y$$
$$z \rightarrow -z$$

as a result of the reflection. Hence for the tensor components we have

$$\left.\begin{array}{l} \alpha_{ii} \rightarrow \quad \alpha_{ii} \\ \alpha_{xy} \rightarrow \quad \alpha_{xy} \\ \alpha_{xz} \rightarrow -\alpha_{xz} \\ \alpha_{yz} \rightarrow -\alpha_{yz} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

The vibrations of the system are divided into those which are symmetrical and those which are antisymmetrical with respect to the plane. (Degeneracy never arises with planes but only with rotation axes and rotation-reflection axes of at least trigonal symmetry.) For symmetrical vibrations we have

$$\alpha_{xz}(q_j) = -\alpha_{xz}(q_j) = 0$$
$$\alpha_{yz}(q_j) = -\alpha_{yz}(q_j) = 0;$$

these components are therefore forbidden for all values of v_j.

For antisymmetrical vibrations

$$\begin{aligned} \alpha_{ii}(q_j) &= \alpha_{ii}(-q_j) \\ \alpha_{xy}(q_j) &= \alpha_{xy}(-q_j) \\ \alpha_{xz}(q_j) &= -\alpha_{xz}(-q_j) \\ \alpha_{yz}(q_j) &= -\alpha_{yz}(-q_j). \end{aligned}$$

Hence for the transitions $\Delta v_j = 0, 2, 4, \ldots$ the quantities α_{xz} and α_{yz} again vanish (cf. (10)), whereas for $\Delta v_j = 1, 3, 5, \ldots$

$$\alpha_{ii} = \alpha_{xy} = 0.$$

From this it follows at once in the latter case that $A_{vv'} = \sum\limits_{ii} (\alpha_{ii})_{vv'} = 0$, so that for vibrations antisymmetrical with respect to the plane (cf. (6), p. 70) the fundamental tone and the even overtones have the depolarization $\frac{3}{4}$. The rules we have deduced may readily be given a physical interpretation also: in the symmetrical vibrations the one principal axis of the α-ellipsoid always remains perpendicular to the plane; in the antisymmetrical vibrations it in general swings out of the plane. The same selection rules also hold for the diagonal axis.

The argument developed here for the plane of symmetry has now to be repeated for all the elements of symmetry and their combinations. The results * are shown in Table I. Before going

* The details of the calculation are given in a paper by the author which will shortly appear in *Ann. d. Physik.*

into these, however, we shall briefly discuss the case of the p-gonal axis of symmetry, in order to exemplify the new features which arise from degenerate vibrations. For the sake of simplicity we shall confine ourselves to fundamental tones ($\Delta v_j = 1$) and consider the degenerate vibrations alone.

The transformation of co-ordinates as a result of rotation is as follows (the axis of symmetry being in the direction of the z-axis):

$$\begin{aligned} x &\to x \cos 2\pi/p + y \sin 2\pi/p \\ y &\to -x \sin 2\pi/p + y \cos 2\pi/p \\ z &\to z. \end{aligned}$$

For suitable combinations of components we then have the following relationships:

$$\left.\begin{aligned} a_{zz} &\to a_{zz} \\ a_{xx} + a_{yy} &\to a_{xx} + a_{yy} \\ a_{xx} - a_{yy} &\to (a_{xx} - a_{yy}) \cos 4\pi/p + 2a_{xy} \sin 4\pi/p \\ a_{xy} &\to \tfrac{1}{2}\{-(a_{xx} - a_{yy}) \sin 4\pi/p + 2a_{xy} \cos 4\pi/p\} \\ a_{xz} &\to a_{xz} \cos 2\pi/p + a_{yz} \sin 2\pi/p \\ a_{yz} &\to -a_{xz} \sin 2\pi/p + a_{yz} \cos 2\pi/p. \end{aligned}\right\} \qquad (12)$$

For the degenerate vibrations for p-gonal axes of symmetry we have the following theorem *: there are always two special forms of vibration such that the ∞^1 general forms of vibration (the degeneracy being double) may be represented by linear combinations of them, which may be chosen in such a way that a rotation of the molecule through the angle $2\pi/p$ is identical with a phase-displacement of $2\pi l/p$ for the first and $-2\pi l/p$ for the second of the two special forms, where l is an integer which can take all values between 0 and p. (The degeneracy arises from the fact that to every vibration with a definite l there corresponds one with $(p - l)$ having the same frequency: the values $l = 0$, $l = p$ correspond to the non-degenerate vibration.)

We write this

$$D^{(1)} \equiv \Phi^{(l)}. \qquad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The above theorem is well illustrated by the degenerate vibration of an equilateral triangle. The forms of vibration for which (13) holds are shown in fig. 1; here the points move in circles.

* Proved in the paper referred to in the footnote on p. 74.

Equation (13), when applied to the polarizability, means that a phase displacement of $2\pi l/p$ must leave the whole ellipsoid unchanged, except for its being rotated through an angle of $2\pi/p$. The resulting selection rules are most easily deduced by putting

$$a_{ik} = c_{ik} \cos (2\pi\nu t - \phi_{ik}). \quad . \quad . \quad . \quad . \quad (14)$$

In order that a component may appear in the Raman effect we must have

$$D^{(1)} a_{ik} = \Phi^{(l)} a_{ik},$$

i.e. the phase displacement of $2\pi l/p$ brought about by (14) must lead to the same result as (12). We see at once that this is not the case for a_{zz} and $a_{xx} + a_{yy}$; these components are therefore forbidden in the Raman effect and hence A vanishes. The depolarization

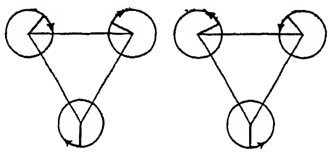


Fig 1

for the degenerate vibrations then amounts to $\frac{3}{4}$ ($\frac{6}{7}$), a fact we made use of in § 2 (p. 68). The application of (13) to the other components leads to further selection rules, which are included in Table I.

In the following table we first give the notation usually employed; this is followed by a description of all the proper functions for the various groups of points arising from a combination of the elements of symmetry.* Each line corresponds to a type of symmetry of proper functions. In the first column the properties of symmetry are given,† in the second the selection rules for all the tensor components,‡ while in the third there follows the degree of depolarization for linearly polarized incident light (possibly to be recalculated by means of (6*a*), (6*b*)), and finally in the fourth the selection rules

* Schönfliess, *Kristallsysteme und Kristallstruktur.*

† Sometimes only by those elements of symmetry which are necessary and sufficient to determine the symmetry completely.

‡ For the applications to molecules, only the depolarization is directly of use; nevertheless, we also give the rules for the separate components, as these become of importance for crystals.

TABLE I*a*

Notation:

σ plane of symmetry.

σ_h plane of symmetry at right angles to an axis.

σ_x plane of symmetry at right angles to x-axis.

σ_v plane of symmetry passing through an axis.

C_p p-gonal axis of symmetry.

S_p p-gonal mirror-rotational axis.

i centre of symmetry.

C_{pv}	C_p and $p\sigma_v$
C_{ph}	C_p and σ_h
D_p	C_p and pC_2 at right angles to C_p
D_{ph}	C_p, σ_h, $p\sigma_v$, and pC_2 at right angles to C_p.
$V = D_2$	$3C_2$ mutually at right angles.
$V_h = D_{2h}$	$3C_2$ mutually at right angles and 3σ through the axes.
S_{pu}	S_p, $\frac{1}{2}p\sigma_v$, and $\frac{1}{2}pC_2$ at right angles to S_p.

s symmetrical, *a* antisymmetrical, *d* degenerate, *f* forbidden.

If any direction is particularly distinguished, it is taken as the z-axis.

	s	*a*	Raman Effect	ρ	Infra-red
1. $C_{1h}(\sigma)$					
A	σ		$c_{xz} = c_{yz} = 0$		$M_z = 0$
B		σ	$c_{ii} = c_{xy} = 0$	$\frac{3}{4}$	$M_x = M_y = 0$
2. C_2					
A	C_2		$c_{xz} = c_{yz} = 0$		$M_z = 0$
B		C_2	$c_{ii} = c_{xy} = 0$	$\frac{3}{4}$	$M_\perp = 0$
3. $S_2(i)$					
A	i				f
B		i	f		
4. C_{2h}					
A_1	C_2, σ_h		$c_{xz} = c_{yz} = 0$		f
A_2	C_2	σ_h	f		$M_\perp = 0$
B_1	σ_h	C_2	f		$M_z = 0$
B_2		C_2, σ_h	$c_{ii} = c_{xy} = 0$	$\frac{3}{4}$	f
5. C_{2v}					
A_1	C_2, σ_x, σ_y		$c_{ik} = 0$		$M_x = M_y = 0$
A_2	C_2	σ_x, σ_y	All zero except c_{xy}	$\frac{3}{4}$	f
B_1	σ_y	C_2, σ_x	,, ,, c_{xz}	$\frac{3}{4}$	$M_x = M_z = 0$
B_2	σ_x	C_2, σ_y	,, ,, c_{yz}	$\frac{3}{4}$	$M_y = M_z = 0$
6. V					
A	$3C_2$		$c_{ik} = 0$		f
B_1	$C_2^{(z)}$	$C_2^{(y)}$, $C_2^{(x)}$	All zero except c_{xy}	$\frac{3}{4}$	$M_x = M_y = 0$
B_2	$C_2^{(y)}$	$C_2^{(z)}$, $C_2^{(x)}$	,, ,, c_{xz}	$\frac{3}{4}$	$M_x = M_z = 0$
B_3	$C_2^{(x)}$	$C_2^{(y)}$, $C_2^{(z)}$	,, ,, c_{yz}	$\frac{3}{4}$	$M_y = M_z = 0$
7. V_h					
A	σ_x, σ_y, σ_z		$c_{ik} = 0$		f
B_1	σ_x, σ_y	σ_z	f		$M_x = M_y = 0$
B_2	σ_z, σ_x	σ_y	f		$M_x = M_z = 0$
B_3	σ_y, σ_z	σ_x	f		$M_y = M_z = 0$
C_1	σ_z	σ_x, σ_y	All zero except c_{xy}	$\frac{3}{4}$	f
C_2	σ_y	σ_z, σ_x	,, ,, c_{xz}	$\frac{3}{4}$	f
C_3	σ_x	σ_y, σ_z	,, ,, c_{yz}	$\frac{3}{4}$	f
D		σ_x, σ_y, σ_z	f		f

TABLE I*b*

	s	a	d	Raman Effect	ρ	Infra-red
8. C_3						
A	C_3			$c_{xx} = c_{yy}, c_{ik} = 0$		$M_\perp = 0$
(d) B			C_3	$c_{xx} = -c_{yy}, c_{zz} = 0$	$\frac{3}{4}$	$M_z = 0$
9. C_{3h}						
A_1	C_3, σ_h			$c_{xx} = c_{yy}, c_{ik} = 0$		f
A_2	C_3	σ_h		f		f
(d) B_1	σ_h		C_3	$c_{xx} = -c_{yy}, c_{zi} = 0$	$\frac{3}{4}$	$M_z = 0$
(d) B_2		σ_h	C_3	$c_{iz} = c_{xy} = 0$	$\frac{3}{4}$	f
10. C_{3v}						
A_1	$C_3, 3\sigma_v$			$c_{xx} = c_{yy}, c_{ik} = 0$		$M_\perp = 0$
A_2	C_3	$3\sigma_v$		f		f
(d) B			$C_3, 3\sigma_v$	$c_{xx} = -c_{yy}, c_{zz} = 0$	$\frac{3}{4}$	$M_z = 0$
11. D_3						
A_1	$C_3, 3C_2$			$c_{xx} = c_{yy}, c_{ik} = 0$		f
A_2	C_3	$3C_2$		f		$M_\perp = 0$
(d) B			$C_3, 3C_2$	$c_{xx} = -c_{yy}, c_{zz} = 0$	$\frac{3}{4}$	$M_z = 0$
12. D_{3h}						
A_1'	C_3, σ_h, σ_v			$c_{xx} = c_{yy}, c_{ik} = 0$		f
A_1''	C_3, σ_v	σ_h		f		$M_\perp = 0$
A_2'	C_3, σ_h	σ_v		f		f
A_2''	C_3	σ_h, σ_v		f		f
(d) B'	σ_h		C_3, σ_v	$c_{xx} = -c_{yy}, c_{zi} = 0$	$\frac{3}{4}$	$M_z = 0$
(d) B''		σ_h	C_3, σ_v	$c_{iz} = c_{xy} = 0$	$\frac{3}{4}$	f

for the infra-red spectrum as deduced by Brester * are given for comparison. The number of proper vibrations associated with the various types depends in each individual case on the number and position of the atoms, and the facts are clearly summarized in the paper previously referred to.† This number is easy to calculate and many data have already been given in Brester's paper.

For reasons of space the table has had to be abbreviated in some respects. In the first place we confine ourselves to Schönfliess'

* C. J. Brester, *Kristallsymmetrie und Reststrahlen*, Dissertation, Utrecht (1923); cf. also *Zeitschr. f. Physik*, **24**, 324 (1924).

These selection rules, which Brester obtained by a rather complicated method, may also be obtained very easily by repeating the above argument with a vector instead of a tensor. We may also mention a paper by Wigner (*Göttinger Nachrichten*, 1930, p. 133), in which Brester's results are obtained with the help of the theory of groups.

† See footnote, p. 74.

crystallographic point-groups (in molecules types of symmetry not included among these are conceivable, e.g. pentagonal or octagonal axes of symmetry; the selection rules for these, however, follow readily from those we have given), and among these we shall omit some groups of the cubical system of which no applications have hitherto been made. In the second place we shall only give the selection rules for fundamental tones. (The corresponding rules for overtones and combination tones may be deduced from these and from what we have said above.) The components of the corresponding tensor are denoted by c_{ik}.

With the help of the table we are now enabled to state the selection rules for the Raman spectrum of a molecule at once without having to investigate the forms of the proper vibrations, which would always be a very troublesome task in the case of a complicated molecule. For some typical applications see § 6 (p. 86).

The polarization rules contained in Table I may also be summarized in a simple way as follows: all vibrations which are degenerate or which are antisymmetrical with respect to any element of symmetry, if not forbidden, correspond to a depolarization of $\frac{3}{4}$. The depolarization of the totally symmetrical vibrations is only determined by the symmetry in the case of T (in general for all groups with cubical symmetry) and is then zero, while in cases of non-cubical symmetry it can take any arbitrary value between 0 and $\frac{3}{4}$. In molecules with an axis of symmetry, moreover, a low degree of depolarization for these vibrations is frequently observed.

It is perhaps useful to render the idea of symmetry used here more precise. The quantities observed, V and α, are determined by the distribution of the outer electrons. Now their symmetry can never be higher, but in certain cases may well be lower, than the symmetry of the nuclear positions as given by X-ray analysis (which depends on the inner electrons). The existence of cases of this kind, however, has not been established with certainty.

Finally, we may mention that the selection rules which have been developed here for harmonic binding also remain strictly valid when the binding is non-harmonic and coupling terms are present. The only case of special interest is where the coupling reaches such a magnitude that quantum numbers can no longer be allotted definitely to the various energy levels. A case like this may occur when two levels happen to degenerate simultaneously, as in the case of CO_2 recently discussed by Fermi * and in that of

* Cf. Rasetti's paper, p. 60.

TABLE I*c*

		s	*a*	*d*	Raman Effect (*a*) $p = 4$	Raman Effect (*b*) $p = 6$	ρ	Infra-red
13. $C_p (p = 4, 6)$	A	C_p			$c_{xx} = c_{yy},\ c_{ik} = 0$	like (*a*)		$M_\perp = 0$
	B		C_p		$c_{xx} = -c_{yy},\ c_{zi} = 0$	f	$(\frac{3}{4})$	f
$(d: l = 1)$	C			C_p	$c_{ii} = c_{xy} = 0$	like (*a*)	$\frac{3}{4}$	$M_z = 0$
$(d: l = 2)$	D			C_p	—	$c_{xx} = -c_{yy},\ c_{zi} = 0$	$\frac{3}{4}$	f
14. C_{ph}	A_1	$C_p,\ \sigma_h$			$c_{xx} = c_{yy},\ c_{ik} = 0$	like (*a*)		f
	A_2	C_p	σ_h		f	f		$M_\perp = 0$
	B_1	σ_h	C_p		$c_{xx} = -c_{yy},\ c_{zi} = 0$	f	$(\frac{3}{4})$	f
	B_2		$C_p,\ \sigma_h$		f	f		f
(*d*)	C_1	σ_h		C_p	f	f		$M_z = 0$
(*d*)	C_2		σ_h	C_p	$c_{ii} = c_{xy} = 0$	like (*a*)	$\frac{3}{4}$	f
(*d*)	D_1	σ_h		C_p	—	$c_{xx} = -c_{yy},\ c_{zi} = 0$	$\frac{3}{4}$	f
(*d*)	D_2		σ_h	C_p	—	f		f
15. C_{pv}	A_1	$C_p,\ p\sigma_v$			$c_{xx} = c_{yy},\ c_{ik} = 0$	like (*a*)		$M_\perp = 0$
	A_2	C_p	$p\sigma_v$		f	f		f
	B_1	$\frac{1}{2}p\sigma_v$	$C_p,\ \frac{1}{2}p\sigma_v'$		All zero except $c_{xx} = -c_{yy}$	f		f
	B_2	$\frac{1}{2}p\sigma_v'$	$C_p,\ \frac{1}{2}p\sigma_v$		,, ,, c_{xy}	f	$(\frac{3}{4})$	f
(*d*)	C			$C_p,\ p\sigma_v$	$c_{ii} = c_{xy} = 0$	like (*a*)	$\frac{3}{4}$	$M_z = 0$
(*d*)	D			$C_p,\ p\sigma_v$	—	$c_{xx} = -c_{yy},\ c_{zi} = 0$	$\frac{3}{4}$	f
16. D_p	A_1	$C_p,\ pC_2$			$c_{xx} = c_{yy},\ c_{ik} = 0$	like (*a*)		f
	A_2	C_p	pC_2		f	f		$M_\perp = 0$
	B_1	$\frac{1}{2}pC_2$	$C_p,\ \frac{1}{2}pC_2'$		All zero except $c_{xx} = -c_{yy}$	f	$(\frac{3}{4})$	f
	B_2	$\frac{1}{2}pC_2'$	$C_p,\ \frac{1}{2}pC_2$		,, ,, c_{xy}	f	$(\frac{3}{4})$	f
(*d*)	C			$C_p,\ pC_2$	$c_{ii} = c_{xy} = 0$	like (*a*)	$\frac{3}{4}$	$M_z = 0$
(*d*)	D			$C_p,\ pC_2$	—	$c_{xx} = -c_{yy},\ c_{zi} = 0$	$\frac{3}{4}$	f

TABLE Ic (continued)

		s	a	d	Raman Effect (a) $p = 4$	Raman Effect (b) [illegible]	p	Infra-red
17. D_{ph}								
	A_1'	C_p, σ_h			$c_{xx} = c_{yy}, c_{ik} = 0$	like (a)		f
	A_1''	$C_p, p\sigma_v$	σ_h		f	f		$M_\perp = 0$
	A_2'	C_p, σ_h	$p\sigma_v$		f	f		f
	A_2''	C_p	$\sigma_h, p\sigma_v$		f	f		f
	B_1'	$\sigma_h, \frac{1}{2}p\sigma_v$	$C_p, \frac{1}{2}p\sigma_v'$		All zero except $c_{xx} = -c_{yy}$	f		f
	B_1''	$\frac{1}{2}p\sigma_v$	$C_p, \sigma_h, \frac{1}{2}p\sigma_v'$		f	f	$(\frac{3}{4})$	f
	B_2'	$\sigma_h, \frac{1}{2}p\sigma_v'$	$C_p, \sigma_v, \frac{1}{2}p\sigma_v$		All zero except c_{xy}	f	$(\frac{3}{4})$	f
	B_2''	$\frac{1}{2}p\sigma_v'$	$C_p, \sigma_h, \frac{1}{2}p\sigma_v$		f	f		f
	C'	σ_h	C_2	$C_p, p\sigma_v$	f	f		$M_z = 0$
(d)	C''		C_2, σ_h	$C_p, p\sigma_v$	$c_{ii} = c_{xy} = 0$	like (a)	$\frac{3}{4}$	f
	D'	C_2, σ_h		$C_p, p\sigma_v$	—	$c_{xx} = -c_{yy}, c_{zi} = 0$	$\frac{3}{4}$	f
	D''	C_2	σ_h	$C_p, p\sigma_v$	—	f		f
18. S_p								
	A	S_p			$c_{xx} = c_{yy}, c_{ik} = 0$	like (a)		f
	B		S_p		$c_{xx} = -c_{yy}, c_{zi} = 0$	f	$(\frac{3}{4})$	$M_\perp = 0$
(d: $l = 1$)	C		$S_2(C_2)$ *	S_p	f	f		$M_z = 0$
(d: $l = 2$)	D	S_2		S_p	—	$c_{xx} = -c_{yy}, c_{zi} = 0$	$\frac{3}{4}$	f
19. S_{pu}								
	A_1	$S_p, \frac{1}{2}pC_2$			$c_{xx} = c_{yy}, c_{ik} = 0$	like (a)		f
	A_2	S_p	$\frac{1}{2}pC_2$		f	f		f
	B_1	$\frac{1}{2}pC_2$	S_p		f	f		f
	B_2		$S_p, \frac{1}{2}pC_2$		f	f		$M_\perp = 0$
(d)	C		$S_2(C_2)$ *	$S_p, \frac{1}{2}pC_2$	f	f		$M_z = 0$
	D	S_2		$S_p, \frac{1}{2}pC_2$	—	$c_{xx} = -c_{yy}, c_{zi} = 0$	$\frac{3}{4}$	f

* The expressions in brackets hold for $p = 4$.

TABLE I*d*

	s	d	Raman Effect	ρ	Infra-red
20. T					
A	$3C_2, 4C_3$		$c_{xx} = c_{yy} = c_{zz}$, $c_{ik} = 0$	0	f
(doubly degenerate) B	$3C_2$	$4C_3$	$c_{ik} = 0$, $c_{xx} + c_{yy} + c_{zz} = 0$	$\frac{3}{4}$	f
(triply degenerate) C		$3C_2, 4C_3$	$c_{xx} + c_{yy} + c_{zz} = 0$	$\frac{3}{4}$	$M_x^2 = M_y^2 = M_z^2$

CCl_4 discussed in § 6, p. 89. Here the coupling gives rise to splitting of the degeneracy. If the transition from a third level (e.g. the fundamental state) to one of the two levels which happen to be degenerate is forbidden in the Raman effect, and that to the other is allowed, then taking account of the coupling has the effect of making a transition to *either* of the split levels (each of which represents a mixture of the two degenerate ones) permissible.* At first sight it would then appear as if any number of cases of accidental degeneracy would always be realized in a complicated molecule with a large number of proper vibrations, and hence the term scheme would be so markedly altered by the splitting thus brought about that a simple description on the basis of normal co-ordinates, like that given here, would no longer have any meaning. This, however, is not so, for the possibilities of such splitting are very closely limited by considerations of symmetry. Thus for example it may be shown that

(1) noticeable splitting can only arise as a result of accidental degeneracies of the type $\nu_j \sim \nu_r + \nu_k$ or $\nu_j \sim 2\nu_k$;

(2) even in these cases it is subject to further special conditions of symmetry.

Molecules with groups which are partially or wholly free to rotate require separate discussion. Here we must return to the integral (2) (p. 67), no longer using the proper functions of the oscillator, but the Mathieu functions corresponding to this problem, as used by Pauling.† Cases of abnormally strong interaction of vibration and rotation may also be dealt with by means of the proper functions given by Teller.‡

* In CO_2 and CCl_4, on the other hand, the transition from the fundamental state to *either* of the degenerate levels is allowed a priori.

† L. Pauling, *Phys. Rev.*, **36**, 430 (1930).

‡ E. Teller and L. Tisza, *Phys. Zeitschr.*, **32**, 219 (1931).

§ 4. Intensity Rules. The Raman Effect and Chemical Binding

According to the above the intensity of the Raman lines depends on two factors. In the first place it depends on the nature of the symmetry of the proper vibration as expressed in the form of the vibration. In last section we investigated under what circumstances the nature of the symmetry causes the intensity to vanish. If we now reverse the question and inquire what symmetries favour particularly large intensities, the answer is: those which give rise to the greatest deviations of the vibration form from the conditions (10), p. 72. For fundamental vibrations, this, as we easily see, is the case when there is symmetry with respect to all the elements of symmetry. The most intense Raman lines accordingly correspond to the " totally symmetrical " vibrations given first in Table I. This is confirmed by experiment in a large number of cases (cf. § 6, p. 86).

Apart from the symmetry, the intensity is determined by the sensitiveness of the polarizability to changes in the distances between the atoms. It is easy to see that in *polar* binding, in which every electron belongs to a definite atom and is subject to the influence of only *one* nucleus, the polarizability is independent of the internuclear distances and no Raman effect can occur. Conversely, a strong Raman effect is to be anticipated with *homopolar* binding; the valency electrons responsible for the chemical binding are also those responsible for the scattering. As they are to all intents and purposes situated in the field of *two* nuclei, the polarizability will depend very much on the distance between these nuclei. These statements are in agreement with a large body of experimental data.*

In order to discuss the transition between these two types of binding,† we may e.g. start with polar binding and work with the idea of the polarizable ion,‡ which has been repeatedly applied in the theory of ordinary light-scattering.§ The classical theory of the Raman effect in diatomic molecules, due to Cabannes and

* P. Krishnamurti, *Ind. Journ. Phys.* **5**, 113 (1930).

† G. Placzek, *Zeitschr. f. Physik*, **70**, 84 (1931).

‡ W. Heisenberg, *Zeitschr. f. Physik*, **26**, 196 (1924); F. Hund, ibid., **31**, 81 (1925); *The Dipole Moment and Chemical Structure* (Leipziger Vorträge, 1929 (Blackie & Son, Ltd., 1931), p. 73.

§ J. Cabannes, *La diffusion moléculaire de la lumière.*

Rocard,* is likewise based on this idea (which, however, is scarcely suitable for diatomic molecules, which are usually homopolar). Just as in the case of ordinary light-scattering, it is possible in the case of the Raman effect also to establish in each particular case by means of polarization experiments how far these or other conceptions do justice to the facts. For a more detailed discussion of the relationships involved here, see the paper referred to in the second footnote on p. 83.

For the chemist it is perhaps useful that he should pay attention to the connexion between the Raman effect and the ideas of molecular refraction frequently applied in organic chemistry. For, as is made clear by the foregoing, the Raman effect is brought about by deviations of the atomic refractions from additivity, which make themselves noticeable even with the very slight changes in the distances between the atoms arising from the vibrations of the atoms within the molecule.

§ 5. The Series for the Polarizability: Fundamental Tones and Overtones

Sometimes it is of advantage to expand the polarizability in terms of normal co-ordinates:

$$\left.\begin{aligned} \alpha = \alpha_0 + \sum_j \left(\frac{\partial \alpha}{\partial q_j}\right)_0 q_j + \tfrac{1}{2} \sum_{jk} \left(\frac{\partial^2 \alpha}{\partial q_j \partial q_k}\right) q_j q_k \\ + \tfrac{1}{6} \sum_{jkl} \left(\frac{\partial^3 \alpha}{\partial q_j \partial q_k \partial q_l}\right)_0 q_j q_k q_l + \ldots \end{aligned}\right\} \quad . \quad . \quad . \quad (15)$$

If we substitute this in (3), p. 68, and form the matrix elements, a number of terms vanish, and we have

$$\alpha_{vv} = \alpha_0 + \tfrac{1}{2} \sum_j \left(\frac{\partial^2 \alpha}{\partial q_j^2}\right)_0 (q_j^2)_{vv} + \ldots = \alpha_0 + \tfrac{1}{2} \sum_j \left(\frac{\partial^2 \alpha}{\partial q_j^2}\right) c_j (2v_j + 1) + \ldots .$$

The term under the sign of summation gives the difference between the polarizabilities of the molecule when at rest in its position of equilibrium and when vibrating.

Similarly

$$\begin{aligned} \alpha_{v_j,\, v_j+1} = \left(\frac{\partial \alpha}{\partial q_j}\right)_0 (q_j)_{v_j,\, v_j+1} + \tfrac{1}{6} \left(\frac{\partial^3 \alpha}{\partial q_j^3}\right)_0 (q_j^3)_{v_j,\, v_j+1} \\ + \tfrac{1}{6} \sum_k \left(\frac{\partial^3 \alpha}{\partial q_j \partial q_k^2}\right)_0 (q_j)_{v_j,\, v_j+1} \cdot (q_k^2)_{v_k v_k} + \ldots \end{aligned}$$

* J. Cabannes and Y. Rocard, *Journ. de Physique*, **10**, 52 (1929).

$$= c_j^{\frac{1}{2}}\sqrt{v_j + 1}\left\{\left(\frac{\partial \alpha}{\partial q_j}\right)_0 + \frac{1}{6}\left(\frac{\partial q_j^3}{\partial^3 \alpha}\right)_0 c_j\,(v_j + 2)\right.$$

$$\left. + \frac{1}{6}\sum_k \left(\frac{\partial^3 \alpha}{\partial q_j\,\partial q_k^2}\right)_0 c_k\,(2v_k + 1)\right\} + \ldots$$

$$\alpha_{v_j,\ v_j+2} = \frac{1}{2}\left(\frac{\partial^2 \alpha}{\partial q_j^2}\right)_0 (q_j^2)_{v_j,\ v_j+2} + \ldots$$

$$= \frac{1}{2}\left(\frac{\partial^2 \alpha}{\partial q_j^2}\right)_0 c_j\sqrt{(v_j + 1)\,(v_j + 2)} + \ldots$$

$$\alpha_{v_j,\ v_j+3} = \frac{1}{6}\left(\frac{\partial^3 \alpha}{\partial q_j^3}\right)_0 (q_j^3)_{v_j,\ v_j+3} + \ldots$$

$$= \frac{1}{6}\left(\frac{\partial^3 \alpha}{\partial q_j^3}\right)_0 c_j^{\frac{3}{2}}\sqrt{(v_j + 1)\,(v_j + 2)\,(v_j + 3)} + \ldots$$

$$\alpha_{v_j,v_j+1;\ v_k,v_k+1} = \frac{1}{2}\left(\frac{\partial^2 \alpha}{\partial q_j\,\partial q_k}\right)_0 (q_j)_{v_j,\ v_j+1}\,(q_k)_{v_k,\ v_k+1} + \ldots$$

$$= \frac{1}{2}\left(\frac{\partial^2 \alpha}{\partial q_j\,\partial q_k}\right)_0 \sqrt{c_j c_k (v_j + 1)\,(v_k + 2)} + \ldots$$

$$c_j = \frac{h}{8\pi^2 \mu_j \nu_j} \text{ (where } \mu_j \text{ is the reduced mass).}$$

Only the odd derivatives enter into the fundamental tone and the even overtones, only the even ones into the undisplaced line and the odd overtones. In addition all the terms of the expansion of order less than n vanish for the nth overtone. Similar statements are true for the combination tones. If we assume that (15) is rapidly convergent, we obtain the well-known rule,* that overtones and combination tones can only appear very feebly in the Raman effect. On the other hand, it would, as is clear from the difference between the selection rules for even and odd overtones, be incorrect to conclude that the fall of intensity in the series of overtones must be regular (the $(n + 1)$th overtone feebler than the nth).

While the selection rules are in general completely independent of the expansion (15), in the degenerate vibrations of systems with trigonal symmetry we have the case † where $(\partial \alpha_{ik}/\partial q_j)_0$ vanishes,

* J. H. van Vleck, *Proc. Nat. Acad. Amer.*, **15**, 754 (1929); C. Manneback, *Zeitschr. f. Physik*, **62**, 224 (1930); G. Placzek, *Zeitschr. f. Physik*, **58**, 585 (1929).

† This, however, does not apply to the rules $c_{zz} = 0$ and $c_{xx} + c_{yy} = 0$, which are strictly true.

but not $(\partial^3\alpha_{ik}/\partial q_j^3)_0$; the contribution to the intensity due to the tensor components indicated as forbidden in the table is therefore of the order of the second overtone. As, however, this has never been observed in the molecules in question, there is no practical difference between the two kinds of selection rules.

§ 6. Applications of the Selection Rules

1. *The group* AB_3.

(*a*) *Pyramid.*—The symmetry is C_{3v}; there are two totally symmetrical vibrations (A) and two degenerate vibrations (B); all the vibrations occur both in the infra-red and in the Raman effect (for the degenerate ones $\rho = \frac{3}{4}$).

To this type belong compounds like PCl_3 and PBr_3; in both there occur four Raman lines, which have been classified on the basis of polarization experiments by Cabannes.*

On the other hand, in the case of NH_3, which may, as the infra-red data have already shown, be represented by the same model, the line 3333·6 alone appears in the gaseous state; this, as is shown by the rotation structure of the corresponding infra-red band,† is associated with a non-degenerate vibration. As owing to the presence of the H nuclei the variation of the polarization with the arrangement of the nuclei will no doubt differ widely from that in PCl_5, say, it is natural to assume from the observations that in the other vibrations the polarizability will be affected only feebly. Nevertheless it should still be possible to observe the corresponding lines (feebly), so that an experimental reinvestigation of NH_3 would be of interest.

Here we may also mention the peculiarity of the term scheme for NH_3, which according to the quantum mechanics must arise when several positions of equilibrium can occur (cf. a paper by Hund).‡ It is possible that a similar case may occur in cyclohexane.

(*b*) *Plane Structure* (central atom at the centre of gravity of an equilateral triangle).—The corresponding point-group is D_{3h}; from Table I we deduce the vibrations and symmetry given in Table II (the number of vibrations is given in the first column).

* J. Cabannes, *Trans. Farad. Soc.*, **25**, 813 (1929).

† G. A. Stinchcomb and E. F. Barker, *Phys. Rev.*, **33**, 305 (1929).

‡ F. Hund, *Zeitschr. f. Physik*, **43**, 805 (1927).

TABLE II

		C_3	σ_h	σ_v	Raman Effect	Infra-red
1	A_1'	s	s	s		f
1	A_1''	s	a	s	f	$M_\perp = 0$
2	B'	d	s	d	$\rho = \frac{3}{4}$	$M_z = 0$

Of the four vibrations, only the totally symmetrical one is allowed in the Raman effect, the others being forbidden. The selection rules may also be interpreted physically: the vibration A_1'' is antisymmetrical with respect to the plane of the triangle, and the position of the ellipsoid relative to this plane can alone vary if the lengths of the principal axes remain constant ($c_{ii} = c_{xy} = 0$). Such a variation, however, is excluded by the symmetry with respect to the trigonal axis, which requires that the ellipsoid should retain its rotational symmetry with respect to this axis. Again, in the degenerate vibrations B' (whose vibration forms may be represented as two combinations of a simple rotation of the carbon atom in the plane with the vibration form of fig. 1, the mixing ratio varying with the particular distribution of force), the ellipsoid must merely appear as if it had rotated through 120° about the trigonal axis (cf. (13), p. 75). We see that this condition can be fulfilled by a rotation of the ellipsoid about its axis with a frequency equal to *half* that of the vibration, and hence (cf. the rotational Raman effect) a frequency double the rotational frequency—i.e. equal to the frequency of vibration—appears in the Raman effect. The strongest line, however, may (§ 4, p. 83) be expected to be the totally symmetrical vibration A (symmetrical contraction of the triangle).

To this type belongs the CO_3 group. Observations on the free ion in solution * have hitherto given only one line 1080, which accordingly corresponds to the vibration A_1'. In calcite crystals the two vibrations B' also appear, but not A_1''. For further details see § 8 (p. 94).

2. *The group* AB_2.

(*a*) *Linear Model.*—Here the forms of vibration and their symmetry (which permits only one of the three vibrations, namely

* M. Leontowitsch, *Zeitschr. f. Physik*, **54**, 155 (1929); R. G. Dickinson and R. T. Dillon, *Proc. Nat. Acad. Amer.*, **15**, 334 (1929).

the totally symmetrical one, to occur in the Raman effect) are well known and no further details need be given here.*

CO_2. Fermi † has shown that accidental degeneracy occurs between the frequencies ν_1 and $2\nu_3$ and that an accurate explanation of the spectrum can be obtained if this fact is taken into account. The assignment of the two strong lines 1285·1 and 1387·8 to ν_1 and $2\nu_3$ given in my paper * must accordingly be modified, seeing that (owing to the accidental degeneracy) each of the two lines corresponds to *both* frequencies.

CS_2. If we make the assumption advocated in my paper,* that $\nu_3 \sim 400$, accidental degeneracy ($\nu_1 \sim 2\nu_3$) again occurs and the interpretation of the CS_2 spectrum (which is entirely analogous to the CO_2 spectrum) can be taken over word for word from that for CO_2. A direct confirmation of these ideas by infra-red measurements of ν_3 would be very desirable.

N_2O. Here accidental degeneracy does not occur ‡ ($\nu_1 = 1317$, $\nu_3 = 450$); the complications which arise in the spectra of CO_2 and CS_2 accordingly do not appear.

(*b*) *Isosceles Triangle.*—The symmetry is C_{2v}; there are two totally symmetrical vibrations and one vibration which is symmetrical with respect to the plane of the triangle but antisymmetrical with respect to the plane at right angles to this. All the vibrations are allowed in the infra-red and in the Raman effect; in the latter $\rho = \frac{3}{4}$.

SO_2. The Raman spectrum confirms the bent structure which has been assumed from dipole moment experiments. It includes three frequencies § (1340, 1146, 526). These are accordingly to be chosen as fundamental frequencies, as was done by Mecke.‖ On the other hand, the classifications of Watson and Parker ¶ and of Bayley, Cassie, and Angus **—who get the value 610 for the third

* Cf. G. Placzek, *Zeitschr. f. Physik*, **70**, 84 (1931). It must be mentioned that the statement of the selection rules given in this paper for the cases discussed in it (which all concern molecules of high symmetry), while adequate and appropriate for that purpose, require to be supplemented in the general case by the results which are summarized in § 3 of the present article (p. 71).

† Cf. Rasetti's paper (p. 60).

‡ C. P. Snow, *Proc. Roy. Soc.*, A, **128**, 294 (1930).

§ S. Bhagavantam, *Ind. Journ. Phys.*, **5**, 35 (1930); R. G. Dickinson and S. S. West, *Phys. Rev.*, **35**, 1126 (1929).

‖ R. Mecke, *Zeitschr. f. Physik*, **64**, 173 (1930).

¶ Watson and Parker, *Phys. Rev.*, **37**, 1484 (1931).

** *Proc. Roy. Soc.*, A, **180**, 142 (1930).

fundamental frequency, the former by ultra-violet work, the latter by infra-red, and who interpret 526 as a combination tone—require alteration. This has recently been confirmed by an observation by Strong.*

Apart from infra-red observations of the rotation structure, the isosceles nature of the SO_2 triangle will only be confirmed if the depolarization of the line 1340 is found to be $\frac{3}{4}$ $(\frac{6}{7})$, so that the measurement of this quantity would be of interest.

3. CCl_4.

The tetrahedral model being assumed, there is one totally symmetrical vibration with $\rho = 0$, and one doubly degenerate and two triply degenerate vibrations, all with $\rho = \frac{3}{4}$ $(\frac{6}{7})$. Among the large number of classifications that of Schaefer † is confirmed by polarization experiments.‡ This also holds for the other tetrahalogen compounds which have been investigated.§ Among these CCl_4 occupies a peculiar position, inasmuch as one of the two lines associated with the triple vibrations (773) splits up into a doublet (758, 789), while in all the analogous compounds the corresponding line is single. The cause of the splitting || is to be sought for in the fact that in CCl_4 an exact accidental degeneracy occurs between the fundamental tone 773 and the combination tone $459 + 314$. As the symmetry condition (cf. § 3, p. 71) is fulfilled (no further details need be given here) this degeneracy leads to splitting of the line. As the intensity measurements carried out by van Wijk and the writer ¶ show, the two components of the doublet have exactly the same intensity, so that the degeneracy is an exact one. Further, the behaviour of the overtone of 773, which occurs in the Raman effect as an extremely feeble line (1539), is of interest. This line has been recorded as single by all the observers. Even special experiments undertaken by van Wijk and the author for this purpose

* J. Strong, *Phys. Rev.*, **37**, 1565 (1931). As Professor Henri has been kind enough to inform me, his recent ultra-violet investigations also lead to the fundamental 526.

† C. Schaefer, *Zeitschr. f. Physik*, **60**, 586 (1930).

‡ J. Cabannes, *Trans. Farad. Soc.*, **25**. 813 (1929); G. Placzek and W. R. van Wijk, *Zeitschr. f. Physik*, **67**, 582 (1931).

§ For further details see G. Placzek, *Zeitschr. f. Physik*, **70**, 84 (1931).

|| An isotope effect is out of the question; as follows from unpublished calculations by Teller, this would not amount to one per cent for the line 773.

¶ G. Placzek and W. R. van Wijk, *Zeitschr. f. Physik*, **67**, 582 (1931).

failed to show any separation. This is in entire agreement with what is to be expected from the conception of accidental degeneracy, for, as we remarked in § 3 (p. 82), it is only accidental degeneracy of the type $\nu_j \sim \nu_k + \nu_l$ that can lead to noticeable splitting, not degeneracy of the type $2\nu_j \sim 2\nu_k + 2\nu_l$, as in the present case.

4. $CHCl_3$.

If one chlorine atom in CCl_4 is replaced by hydrogen, the symmetry is altered from T to C_{3v}. There are three totally symmetrical vibrations (A) and three triply degenerate vibrations (B); for the latter, as for all cases of degenerate vibration, $\rho = \frac{3}{4}\left(\frac{6}{7}\right)$. We may think of the $CHCl_3$ spectrum as derived from that of CCl_4 by displacement of the single and double CCl_4 frequencies and splitting of each of the two triple ones into a single one and a double one. Hanle's experiments * with circularly polarized incident light enable the details of the transition to be followed. He finds that three of the six lines are "correct" and three are "reversed" (the latter corresponding to the degenerate frequencies). The totally symmetrical CCl_4 frequency 459 becomes 668, the double 219 becomes 259, the triple 314 and 773 split up into the double 366 and 761 and the single 1222 and 3025. The two additional feeble lines 1441 and 3072 found in the spectrum of $CHCl_3$ by Dabadghao † are to be interpreted as overtones or combination tones.

5. CH_2Cl_2.

If another chlorine atom is replaced by hydrogen the symmetry becomes C_{2v}; the symmetry of the vibrations is given in Table III. All the degeneracies are split up, so that the observed spectrum ‡ contains an extremely large number of lines.

For a detailed classification polarization experiments are necessary, but these have not yet been completed. When these data are available we shall be able to explain the whole variation of the vibration terms from CCl_4 to CH_4 (CH_3Cl is analogous to chloroform so far as symmetry is concerned and has already been investigated sufficiently in the infra-red).

* W. Hanle, *Naturwiss.*, **19**, 375 (1931); *Phys. Zeitschr.*, **32**, 556 (1931).

† W. M. Dabadghao, *Ind. Journ. Phys.*, **5**, 207 (1930).

‡ A. Dadieu and K. W. F. Kohlrausch, *Sitzungsber. d. Wiener Akad.* (II*a*), **139**, 165, 717 (1930).

TABLE III

		C_2	σ_x	σ_y	Raman Effect	Infra-red
4	A_1	s	s	s		$M_z \neq 0$
1	A_2	s	a	a	$\rho = \frac{3}{4}$	f
2	B_1	a	a	s	$\rho = \frac{3}{4}$	$M_y \neq 0$
2	B_2	a	s	a	$\rho = \frac{3}{4}$	$M_x \neq 0$

6. *Benzene.*

If, as usual, a plane structure is assumed for benzene, the symmetry is D_{6h}. We see at once (Table I) that for this type of symmetry all the Raman lines must be forbidden in the infra-red and vice versa. In reality, however, this is far from being the case, a large number of the Raman frequencies being also observed in the infra-red.* The same alternatives † apply to a model with symmetry S_{6u} (e.g. with hydrogen nuclei alternately above and below the carbon ring, which may also be bent), which was previously considered more probable by Bragg in view of X-ray data.

On the other hand, agreement with the facts is obtained if we assume that the hydrogen atoms form a hexagon which does not lie in the plane of the carbon hexagon, so that the symmetry falls to C_{6v}. (All the hydrogen atoms may be above carbon atoms, or, what is more probable, each hydrogen atom may be half-way between two carbon atoms, but out of the plane of the latter.)

The most intense lines may be classified independently of assumptions about the position of the hydrogen atoms; thus, for example, the line 992 corresponds to symmetrical contraction of the benzene ring. In addition it may be mentioned that the attempts at classification hitherto made by various writers * contravene the simplest selection rules, and are therefore not worth considering.

§ 7. The Distribution of Intensity in the Raman Lines

The above considerations all refer (as was emphasized at the beginning) to the total intensity of a Raman line, which is in general composed of the pure vibration line (Q-branch) and the rotation

* Cf. e.g. the summary given by S. Bhagavantam, *Ind. Journ. Phys.*, **5**, 615 (1930); see also R. C. Yates, *Phys. Rev.*, **36**, 563 (1920); Kettering, Shutts, and Andrews, *Phys. Rev.*, **36**, 531 (1930).

† It may be shown, moreover, that this fact still holds when accidental degeneracy is taken into account.

branches. We see at once without any calculation that if $\gamma_{vv'}$, the anisotropy of the tensor $(a)_{vv'} = (\Delta a)_{vv'}$ which is characteristic of the transition $v \rightarrow v'$, vanishes, the change in the polarizability associated with the vibration is independent of the orientation of the molecule and hence cannot be affected by rotation, so that in this case rotation branches cannot occur. This is the reason for the fact, which has frequently been emphasized, that markedly polarized lines are always very sharp, while markedly depolarized lines are broadened out.

If we wish to obtain the intensities of the separate branches by themselves, we have to modify the averaging process of § 2 (p. 68) somewhat. The tensor $(\Delta a)_{vv'}$ may be decomposed into a number of tensors, each of which is characteristic of a separate rotation branch. The ellipsoids corresponding to these tensors, however, are no longer at rest in the molecule, but in space; they are symmetrical about the axis of total angular momentum. The averaging over all possible directions of the latter in space is formally identical with that carried out in § 2 (p. 68), and leads to the expressions (5), but now the quantities A and γ refer to one branch separately.* It must be pointed out that in polyatomic molecules the quantum number of the total angular momentum (J) is not, as in the case of diatomic molecules, subject to the selection rule $\Delta J = 0, \pm 2$ for the Raman effect; in general $\Delta J = \pm 1$ is also permissible.

For extremely low temperatures (or extremely small moments of inertia, as in H_2) the averaging must be replaced by summation over the rotational levels, and azimuthal quantization (magnetic quantum number).

Calculations of this kind have been carried out by Teller and the author;† for diatomic molecules the problem has already been solved in another way by Manneback ‡ (starting from the Kramers-Heisenberg formula).

§ 8. The Raman Effect in Crystals

In order to apply the selection and polarization rules to crystals we must investigate the effect of the additional elements of symmetry

* From this it follows at once that formula (6), p. 70, is true not only for the total intensity, but also for each branch alone. It likewise holds for each rotation line separately.

† See a paper by G. Placzek and E. Teller, which will shortly be published in *Zeitschr. f. Physik.*

‡ W. M. Dabadghao, *Ind. Journ. Phys.*, 5, 207 (1930).

(translation, screw axes, glide-reflection planes) which arise here. It is found that these lead to a relationship between the vectors of light waves and elastic waves, which is analogous to Bragg's relationship and which has already been obtained in another way by Landsberg, Leontowitsch, Mandelstamm,* and Tamm.† This relationship enables us, if we confine ourselves to fundamental tones, to regard the Raman effect to a good approximation as caused merely by those vibration forms of the lattice which consist solely of vibrations of the separate rigid lattices relative to one another. Now, as Brester ‡ has shown, it is possible to assign to each crystal lattice a finite point system whose vibrations have the same properties of symmetry as those lattice vibrations which are of the type just mentioned. As these can alone occur in the Raman effect, we may accordingly obtain the selection and polarization rules by investigating the vibrations of this corresponding point system. Here, of course, the averaging over various orientations in space is no longer required, and the polarization of the scattered radiation follows directly from the selection rules for the individual tensor components. The symmetry of the point system is that of the point-group isomorphous § with the space group of the crystal; it contains as many particles as the basis of the crystal.

We shall briefly illustrate this in the single case of calcite, without giving an exhaustive discussion of the numerous interesting problems which arise in this particular case.||

The symmetry of the corresponding point system is S_{6u} (cf. Brester, loc. cit.); the vibrations are shown in Table IV (cf. also Table I, p. 77 *et seq.*).

As the basis of the calcite lattice consists of *two* $CaCO_3$ molecules, eight of the vibrations of Table IV are vibrations of the CO_3 group already discussed in § 6 (p. 87). These nearly coincide in pairs; to the symmetrical vibration of the ion there correspond two vibrations of type A_1 and B_1, both forbidden in the infra-red and the

* Landsberg, Leontowitsch, and Mandelstamm, *Zeitschr. f. Physik*, **60**, 334 (1930).

† I. Tamm, *Zeitschr. f. Physik*, **60**, 345 (1930).

‡ C. J. Brester, *Kristallsymmetrie und Reststrahlen*, Dissertation, Utrecht (1923); cf. also *Zeitschr. f. Physik*, **24**, 324 (1924).

§ For the conception of isomorphism see Schonfliess, *Kristallsysteme und Kristallstruktur*.

|| The discussion of the CO_3 group and of calcite given in the German version of this paper contained some errors, which have been corrected here. I am indebted to Professor Fermi for having pointed them out to me.

TABLE IV

		Raman Effect	Infra-red	Internal (CO_3) Vibrations	External (Lattice) Vibrations
1	A_1	$c_{xx} = c_{yy};\ c_{ik} = 0$	f	1	0
3	A_2	f	f	1	2
2	B_1	f	f	1	1
3	B_2	f	$M_\perp = 0$	1	2
5	C	f	$M_\perp = 0$	2	3
4	D	$c_{xx} = -c_{xy};\ c_{zi} = 0$	f	2	2

former active in the Raman effect. To the vibration which is antisymmetrical with respect to the CO_3 plane, there correspond two vibrations of type A_2 and B_2, both forbidden in the Raman effect, and the latter active in the infra-red. Finally, each of the two degenerate CO_3 vibrations is composed of two vibrations C and D, likewise degenerate (C Raman-inactive, infra-red-active; D Raman-active, infra-red-inactive). The selection rules are accordingly identical with those for the free ion, with the sole distinction that for the two degenerate vibrations in the latter case no exact agreement between the Raman lines and the corresponding infra-red bands is to be expected, but on the contrary there occurs a small difference of frequency of an order of magnitude corresponding to the energy of interaction of one CO_3 group with the other or with the lattice.

In the scattered spectrum of calcite * by far the strongest line is 1088, which is exactly the same as the frequency found for the free ion and is to be ascribed to the symmetrical vibration; the antisymmetrical frequency, whose value is known from the infra-red spectrum to be 880,† is absent, in accordance with the selection rule. To the two degenerate vibrations there correspond the lines 714 and 1438; it does not appear certain whether the accuracy with which the corresponding infra-red bands are known is sufficient to establish a difference of frequency of the kind mentioned. These bands, moreover, have been recorded as double by Schaefer and Schubert,† and Brester and Schaefer thence conclude that in the crystal there is a deviation from the trigonal symmetry of the CO_3 group. This conclusion, however, is not supported by the Raman spectrum.

After the CO_3 vibrations have been dealt with there still remain

* C. Schaefer and fellow-workers, *Zeitschr. f. Physik*, 65, 280 (1930).

† Cf. Schaefer and Mattossi, *Das ultrarote Spektrum*.

ten low-frequency lattice vibrations, the distribution of which is given in Table IV. Of these only the two vibrations D are permitted in the Raman effect; this is in complete agreement with experiment, which gives only the two lines 155 and 282 in the low-frequency region of the scattered spectrum. In the infra-red these two vibrations are forbidden, and they have not been observed either.

So far as polarization experiments are concerned, there are still considerable discrepancies between the results of Schaefer * and Cabannes.† The conclusions which Leontowitsch ‡ and Mattossi § draw from the experiments are based on the theory of Leontowitsch, which deviates from that given above and which will be discussed elsewhere.

§ 9. Methods for investigating Structure

In view of the above considerations the following process would seem to be the most suitable for investigations of molecular structure. The first step is the experimental determination of the frequencies and polarization of the Raman lines. Once this is carried out, the next thing is to ascertain which type of symmetry in the structure of the molecule (if more than one can occur) is in agreement with the scattered spectrum, the infra-red data being always kept in mind. Starting from the general rules for intensity, polarization, and selection, we then proceed to determine the fundamental frequencies, at first without any assumptions about the forces. In many cases the problem can be completely solved in this way, while in others alternatives will still exist. In the latter case considerations based on models may be used to deduce a rough idea of the probable positions of the frequencies, the arbitrariness inherent in this procedure being considerably reduced owing to the limitation of the possibilities by considerations of symmetry.

When the scheme of levels for the vibrations has been obtained in this way, it is possible in simple cases to calculate the relationships between the fundamental frequencies which result from particular assumptions about the forces, for various simple assumptions (e.g. a central force system ‖ and a valency force system ¶). From

* C. Schaefer and fellow-workers, *Zeitschr. f. Physik*, **65**, 280 (1930).

† J. Cabannes, *La diffusion moléculaire de la lumière*.

‡ M. Leontowitsch, *Zeitschr. f. Physik*, **61**, 548 (1930).

§ F. Mattossi, *Zeitschr. f. Physik*, **64**, 34 (1930).

‖ Cf. D. M. Dennison, *Reviews of Modern Physics*, **3**, 280 (1931).

¶ Cf. the report by K. W. F. Kohlrausch, *Phys. Zeitschr.*, **32**, 385 (1931).

the deviations of these from the experimental relationships interesting and reliable conclusions may be drawn about the chemical binding.

The great importance of the depolarization has been made sufficiently apparent by the foregoing. Hence the Raman investigations which will at the moment be most effective in advancing our knowledge of molecular structure are polarization experiments. Here, however, it must be forcibly emphasized that for deciding questions of classification only those quantitative experiments are of use in which the curve of blackening of the photographic plate is correctly determined. No conclusions of any kind can be drawn from data obtained by methods like e.g. that used by Bhagavantam * (in which mercury spectra obtained with various exposures were used instead of blackenings, and polarization due to the apparatus was corrected for by prolonging the exposure of one component by a constant factor). On the other hand, the use of parallel incident light, which for feeble lines increases the exposure very much, may if necessary be avoided by the procedure worked out by van Wijk and the author.†

Note.—In the deduction of the selection rules for vibrations degenerating to a trigonal axis, which are regarded in the text (p. 86) as approximately valid ($\partial\alpha/\partial q = 0$, $\partial^3\alpha/\partial q^3 \neq 0$), an error has crept in. The rotation of the ellipsoid about the z-axis discussed in the example of § 6, 1(*b*) (the CO_3 group) may without destroying the symmetry take place with *half* the vibration frequency, so that this frequency appears in the Raman effect in the *first* approximation and not merely in the third.

Hence for the *free* CO_3 ion *three* Raman frequencies are to be anticipated instead of one, one of them (the totally symmetrical one) being very intense. On the other hand, the discussion of the Raman effect of the CO_3 group in the *crystal* (§ 8) is unaffected by this, owing to the higher symmetry (S_{6u}) of the corresponding point system.

* Bhagavantam, *Ind. Journ. Phys.*, **5**, 59 (1930).

† G. Placzek and W. R. van Wijk, *Zeitschr. f. Physik*, **67**, 582 (1931).

Band Spectra and Dissociation

Miss H. SPONER, Göttingen

Introduction

A molecule may execute three types of internal motion: (1) it may rotate as a whole about its centre of gravity; (2) the nuclei of its constituents may vibrate relative to one another (in diatomic molecules the nuclei of the two atoms, in polyatomic molecules possibly groups of nuclei); and (3) the electrons may move. As is well known, the molecular rotation is manifested optically by the so-called rotation spectrum, which lies in the remote infra-red; the combination of nuclear vibration and rotation gives the rotation-vibration spectra, which are also found in the infra-red; if there is an electronic jump in addition we speak of electronic bands, which may occur anywhere from the visible region (or possibly from the infra-red) to the far ultra-violet.

The question now arises, can these motions be so amplified as a result of light absorption as to cause dissociation of the molecule? This problem and others will be discussed with reference to diatomic molecules, as meanwhile it is only in this case that definite information is available. We first consider rotation of a molecule brought about by receipt of rotational energy. Suppose that the molecule is in the normal state of electronic motion and nuclear vibration. In theory any adequate supply of energy should give rise to dissociation, i.e. should be able to give the molecule so much energy that the centrifugal force reaches a value corresponding to the energy of dissociation. In practice, however, absorption of light does not lead to a splitting-up of the molecule, as in molecules with an electric moment only one rotational quantum can be absorbed and the rotational energy of molecules without an electric moment cannot be increased by absorption at all.

We shall now consider the possibility of dissociation arising from a supply of vibrational energy. We assume that the electronic system of the molecule is in the normal state. Whether the rotation

is in the normal state is of no consequence in this connexion. In this case it is again theoretically possible to enhance the vibrations so much (e.g. by raising the temperature) that the molecule is split up into two atoms. It is otherwise when we attempt to realize this by absorption of light. The vibrational energy of a non-polar molecule cannot be enhanced at all in this way, as the molecule possesses no electric moment. A polar molecule may be regarded as an anharmonic oscillator. A system of this kind can in theory absorb more than one vibration quantum, but the intensity decreases so rapidly as the change of the vibrational quantum number increases that practically only the first few vibrations are absorbed. This means that absorption of vibrational energy cannot lead to dissociation. Stepwise absorption up to the stage of dissociation, though conceivable, cannot be realized in practice.

As a third case we consider the dissociation of a molecule by simultaneous supply of electronic energy and vibrational energy. Here we overlook the simultaneous transference of rotational energy, which we shall consider later. This third case is the one which can be realized in practice by means of light absorption, for here any number of vibrational quanta are transferred in one action at the same time as an electron jump takes place. In order to summarize the relationships in a convenient form we use the well-known potential curves in which the potential energy of the mutual action of the nuclei is plotted as a function of the distance between them.

The Franck-Condon Principle

By considering potential curves Franck * deduced a very important principle which gives the intensity distribution in band spectra. This principle, which he stated qualitatively, was expressed in a quantitative form by Condon, † using the new quantum mechanics. The train of thought is somewhat as follows.

We consider a molecule with the two potential curves shown in fig. 1. Let the lower curve represent the fundamental state. Absorption of light causes the molecule to pass into the excited electronic state represented by the upper curve. The electronic jump is a very rapid process. Although the system of the light electrons is thereby altered, the relative positions of the heavy nuclei

* J. Franck, *Trans. Farad. Soc.*, **21**, 536 (1925).

† E. U. Condon, *Phys. Rev.*, **28**, 1182 (1926); **32**, 858 (1928).

cannot alter during the transition. During this time they receive potential energy only; after the act of absorption this is periodically transformed into kinetic energy. In the first instant of absorption, then, the molecule passes from a state on the lower potential curve to a state vertically above it on the upper potential curve. Such transitions are indicated in the figure by vertical lines. According to quantum mechanics there is no state in which a molecule does not vibrate, but each molecule possesses a so-called zero-point vibration.* Hence the internuclear distance cannot be determined by definite points but is represented by a probability curve. The maximum probability in the state of zero-point energy is at the

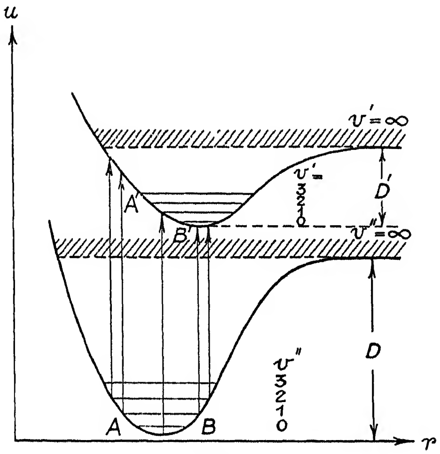


Fig. 1

minimum of the curve. In this state, therefore, absorption takes place preferably from the minimum. The probability that the nuclei will be found at a given distance apart falls off exponentially on either side. What we obtain, therefore, is not a transition merely from a given point on one potential curve to a given point on the other potential curve, but a broad region with a maximum at the place where, according to ordinary mechanics, a transition would alone take place. In the first state of vibration we no longer have a simple Gaussian error curve for the internuclear distance (see the dotted curve in fig. 2) but a curve of the form shown, since the ψ function for this state possesses a node.

* The zero-point vibration is of the order of half a vibrational quantum, so that the vibrational quantum numbers are multiples of $\frac{1}{2}$, $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$, &c. Whole numbers are used in fig. 1 for the sake of simplicity.

The loops of the vibration lie at the turning-points, e.g. A and B in the figure. These are the places where transitions are most likely to occur, in view of the idea that the velocity of the nuclear motion is least at the turning-points, and hence the probability is greatest there that the absorbed radiation will meet the molecule exactly at one of these points. If we carry out absorption experiments at high temperatures, that is, if we excite new vibrations in the molecule, additional nodes occur in the proper functions. Absorption is still most probable at the turning-points, but there is also a finite possibility of the radiation meeting the molecule at an intermediate state in its vibration. As the excited state for the various vibrations also possesses proper functions with a number of nodes and loops,

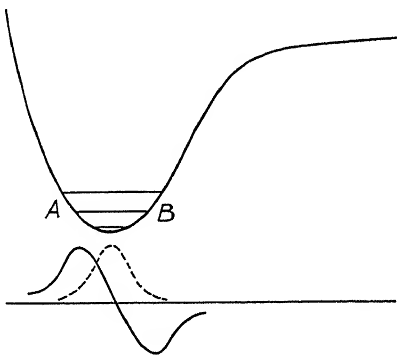


Fig 2

it may happen in the transition that these nodes and loops exactly coincide and thus give rise to variations of intensity in a vibration series. For example, the variations in intensity first found by R. W. Wood in the resonance doublet series of iodine probably arise in this way. Using the green mercury line he excited 28 close doublets, whose intensities, starting with that of the green line causing the excitation, are approximately as follows: 10, 9, 1, 9, 3, 8, 8, 2, 9, 0, 8, 3, 2, 7, 0, 7, 0, 2, 1, 0. Years ago Lenz * attempted to explain this variation by considerations of correspondence. That the variation has nothing to do with rotation in any way was suspected by Pringsheim † and has now been proved by Cario in Göttingen. He first excited the resonance series with quite sharp lines, that is, selected a definite rotation term, and then used broader lines,

* W. Lenz, *Zeitschr. f. Physik*, **25**, 299 (1924).

† P. Pringsheim, *Fluoreszenz und Phosphoreszenz*, 3rd ed., p. 53

which excited a number of rotational quanta simultaneously. It was found that in these cases the same bands are strong or weak over the whole range. By exact measurements of intensity under definite conditions Cario hopes to be able to infer the beats in the proper functions.

Bearing in mind the Franck-Condon principle which we have just discussed, we at once recognize the cause of the varying structure of molecular spectra. Fig. 3*a* represents the potential curves of a molecule in which the internuclear distance and the strength of binding are practically the same in the fundamental state and in the excited state.

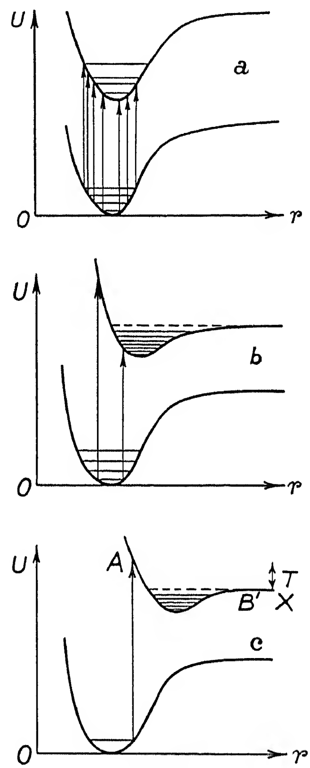


Fig 3

The bands chiefly represented in the spectrum of this molecule will be those for which the state of vibration remains unaltered (0—0, 1—1), i.e. those corresponding to the diagonal terms in the quadratic vibration diagrams. This is exemplified by the molecules CN, SiN. Fig. 3*b* represents a molecule which is rigidly bound in the fundamental state and loosely bound in the excited state (the halogens, hydrogen). In the spectrum those bands for which the change in the vibrational quantum number is large must chiefly occur. As the curve representing the higher state is rising steeply at a place where the lower curve is still flat, we may expect long series of bands leading from a lower state in which the vibrations are largely independent to a series of strongly vibrating upper states or even to a continuous region. Still more extreme relationships hold in fig. 3*c*. The vertical passage from the fundamental state with zero-point vibration here leads to a point on the upper curve which lies above the limit of dissociation. Hence on absorption the molecule dissociates, which is shown spectroscopically by a purely continuous absorption region. Continuous regions, of course, always occur when absorption leads to a repulsion curve. The existence of potential curves of this type, which correspond to

a permanent repulsion of the atoms, was first suggested on theoretical grounds by Heitler and London * and has since been observed. A transition to a repulsion curve is known to occur in emission in hydrogen. Blackett and Franck † had already suspected that the ultra-violet continuous spectrum of hydrogen is caused by a transition into a dissociated state, and Winans and Stueckelberg ‡ interpreted it as due to transitions from excited states to the lowest state of the triplet system $^3\Sigma$, which corresponds to a repulsion. In absorption, transitions to repulsion curves have been definitely observed in the methyl halides § and in the halogens. ||

Determination of Energies of Dissociation

As will be seen from the foregoing, the most favourable case for the determination of the vibration term system and the dissociation—a long succession of bands, finally converging and merging into a continuous spectrum—only occurs under quite definite conditions as regards potential. Most molecules only give the first few bands sufficiently intensely, or else the continuous spectrum only. As regards the halogens, for example, it is only in the case of iodine that the whole series of bands and the continuous spectrum are strongly developed; in bromine, and still more in chlorine, the maximum of absorption is well into the continuous spectrum and the bands appear only feebly. If a more or less long series of bands is alone observed, we can find the position of the convergence limit by extrapolation, using the law of decrease of the vibrational quanta with increase of quantum number. ¶ The value of the method of course depends very largely on the magnitude of the extrapolation. In homopolar compounds it is found that the vibrational quanta very frequently decrease linearly with the quantum number to a first approximation. The method is not applicable to heteropolar compounds. Kratzer ** has in fact shown that when the internuclear distance is large and the power series for the law of force begins with a term $1/r^2$ or $1/r^3$, the maximum amount of vibrational

* W. Heitler and F. London, *Zeitschr. f. Physik*, **44**, 455 (1927).

† P. M. S. Blackett and J. Franck, *Zeitschr. f. Physik*, **34**, 389 (1925).

‡ J. G. Winans and E. C. G. Stueckelberg, *Proc. Nat. Acad. Amer.*, **14**, 876 (1928).

§ G. Herzberg and G. Scheibe, *Zeitschr. f. phys. Chemie*, B, **7**, 390 (1930).

|| H. Cordes and H. Sponer, *Zeitschr. f. Physik*, **63**, 334 (1930).

¶ R. T. Birge and H. Sponer, *Phys. Rev.*, **28**, 260 (1926).

** A. Kratzer, *Zeitschr. f. Physik*, **26**, 40 (1925).

energy to be taken up is finite, but the corresponding vibrational quantum number becomes infinite. This is the case for ionic molecules. The curve (*a*) in fig. 4 represents the vibrational quantum as a function of the vibrational quantum number (here denoted by n).

At first the slope of the curve may even decrease; subsequently, however, there must be a point of inflection and the curve must run as shown in the figure. If, however, the power series begins with $1/r^4$ or terms with higher exponents, the maximum vibrational energy and quantum number are finite. This means that even

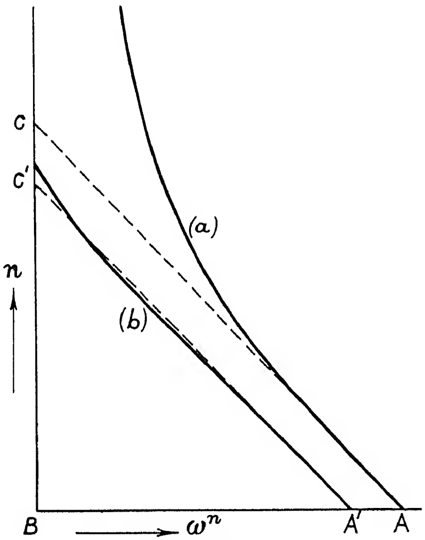


Fig. 4

if the curve is concave upwards at first, it must in the end intersect the n-ordinate (see e.g. curve (*b*)). As for atomic molecules in which the distance between the nuclei is large the expression for the law of force probably begins with $1/r^9$, the curve in this case is of type (*b*).

The magnitude of the energy of dissociation may also be estimated with some degree of accuracy from the position of the continuous spectrum. The long-wave end of the continuous spectrum lies beyond the convergence limit and gives an upper limit for the energy of dissociation.* In the cases where the molecule decomposes into a normal atom and an excited (non-metastable) atom, we often

* J. Franck, H. Kuhn, and G. Rollefson, *Zeitschr. f. Physik*, **43**, 155 (1927).

proceed by observing not the long-wave limit of absorption but the fluorescence produced by the return of the excited atom to the fundamental state.* The longest incident wave-length which still gives atomic fluorescence then corresponds to the long-wave boundary of the continuous region of absorption.

Results on Chemical Binding

(*a*) *Ionic Molecules.*

In what follows we shall give some details of the results on chemical binding which can be obtained from experimental spectroscopy, and information about the products into which the various molecular states dissociate, i.e. what correlations of molecular terms with separate atomic terms are suggested by experiment.

Abegg defined a homopolar compound as one which is built up of atoms, a heteropolar compound as one which is built up of ions. To-day the terms polar and non-polar are largely used in these senses or to denote whether a molecule dissociates into ions in solution or not. On the other hand, however, the expressions polar and non-polar are frequently used to define the distribution of charge in a molecule. Franck † accordingly proposed the terms atomic compound and ionic compound for use when it is desirable to classify a molecule according to the constituents into which it decomposes adiabatically (with respect to the system of electrons). For this purpose he defined an ionic compound as a molecule which if its vibrations in the fundamental state were increased would dissociate into two ions with equal and opposite charges. An atomic compound, on the other hand, would in the fundamental state give two atoms as products of dissociation. If, however, we are concerned with the distribution of charge in the complete molecule, the terms polar and non-polar are entirely justifiable. There would accordingly be polar and non-polar atomic compounds.

What data does experiment provide as a test of the definition? We can in the first place take emission spectra, i.e. trace out the series of vibrational quanta of the fundamental state to the convergent limit, or extrapolate to the latter and see whether it leads to a dissociation into atoms or into ions. Secondly, we can study the processes of absorption, i.e. the series of vibrational quanta in the excited state, and look for laws applying to atomic molecules and

* A. Terenin, *Zeitschr. f. Physik*, **37**, 98 (1926).

† See e.g. J. Franck, *Naturwiss.*, **19**, 217 (1931).

ionic molecules. We first consider ionic molecules. The convergence limit of the vibration terms in the fundamental state should give a decomposition into ions. Here, therefore, the electronic state whose system of vibrations in the limit leads to normal atoms is not the most stable, and is accordingly an excited state of the ionic molecule. As the ionization potentials are usually large compared with the electronic affinities, the convergence limits of the fundamental states lie very high and their potential curves are

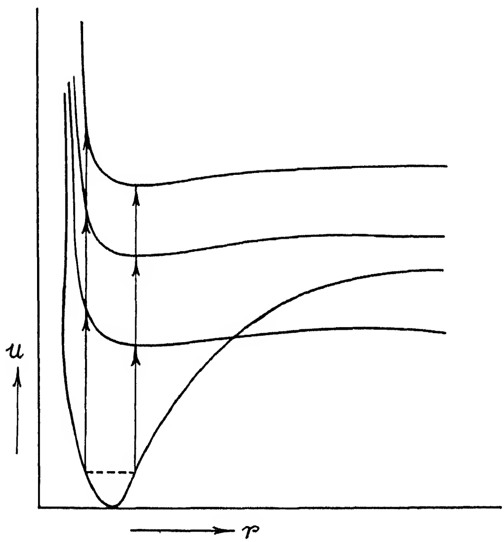


Fig. 5

usually intersected by those of excited states. The following example is typical of the potential curves of an ionic molecule (fig. 5).

The potential curve of the first excited state cuts that of the fundamental state. From the theoretical side this intersection has been objected to on the grounds that the proper value is degenerate and that in adiabatic changes the continuing of an energy curve through a point of degeneracy has no meaning. There is indeed no difficulty when the intersecting terms are of different natures. The nature of a term cannot be altered adiabatically. In this case, therefore, the path through the point of degeneracy is unique. In the alkali halides, however, it is not certain whether terms of different natures occur. The fundamental state leads to a positive alkali ion and a negative halogen ion, and hence to forms resembling

an inert gas; that is, the atomic ions are in ^{1}S-states and the molecule is certainly in a $^1\Sigma$-state.

The first state of excitation gives an alkali atom in the ^{2}S-state and a halogen atom in the ^{2}P-state, that is, it could be a $^1\Sigma$-term or a $^1\Pi$-term. Does the intersection of the terms have a meaning, then, when a $^1\Sigma$—$^1\Sigma$ transition is concerned? I should first like to point out that from the experimental point of view the question can be answered in the affirmative.

The magnitude of the fundamental vibration quanta, i.e. the lower limit of the potential curve, is known from investigations by Sommermeyer.* In the case of the molecules of the alkali halides, indeed, no really discrete band spectra have been observed, but the continuous regions exhibit regular variations of intensity. These are to be interpreted as maxima of the probability of transition,† that is, they have nothing to do with bands caused by discrete quantum transitions. The occurrence of these fluctuations, which appear like diffuse bands, can be explained by means of the potential curves. The potential curves of excited states may have a slight inclination to the horizontal as shown in fig. 5. The most probable transitions for one of the lower states of vibration are indicated in the figure. In transitions represented by the right-hand arrow a definite uncertainty in the value of r gives rise only to a slight uncertainty in the value of the frequency, owing to the flatness of the upper curve. Here, therefore, there is a very narrow maximum of absorption, in contradistinction to the transitions represented by the left-hand arrow, which give a continuous spectrum. The transitions from the different states of vibration give a series of such maxima, which manifest themselves as fluctuations of intensity on a continuous background. If the inclination of the upper potential curve is neglected the distances between the fluctuations give the vibrational quanta of the fundamental state. The fundamental vibrational quanta which have been measured by Sommermeyer by this method for a series of alkali halides agree with the values calculated by Born and Heisenberg ‡ and van Leeuwen § within the limits of experimental and theoretical error. The course of the end of the curve is known by calculation. On the

* K. Sommermeyer, *Zeitschr. f. Physik*, **56**, 548 (1929).

† H. Kuhn, *Zeitschr. f. Physik*, **63**, 458 (1930).

‡ M. Born and W. Heisenberg, *Zeitschr. f. Physik*, **23**, 388 (1924).

§ H. J. van Leeuwen, *Zeitschr. f. Physik*, **66**, 241 (1930).

side to which they diverge the fluctuations of intensity pass into a continuous region of strong absorption, which for low vapour densities is by far the most striking part of the phenomenon. Of these regions of continuous absorption that of longest wave-length corresponds to dissociation into normal atoms, while those of shorter wave-length give excited dissociation products. In a number of cases, in fact, it is possible to associate a definite dissociation process with each continuous region by means of the distances between the maxima of the various continuous regions of absorption. It is found that excitation of the alkali atoms as well as of the halogen atoms occurs, as is shown by the table on p. 108.*

The higher stages of excitation of course give a broad irresolvable region of absorption. From the fact that the distances between the maxima of the continuous regions correspond very nearly to the stages of excitation of the atoms, it follows that the potential curves of the excited states run approximately parallel to one another. The loose binding, and hence the flat potential maximum of the excitation states, follows from the observations of regions of absorption which are practically continuous.

It has been objected that the potential curve of the fundamental state might be the $^1\Sigma$-curve, which in the limit leads to normal atoms (this would mean that the alkali halides would have to be reckoned as atomic molecules) and that the curve of the first excited state is the $^1\Pi$-curve, which would mean that the curves do not intersect. This, although not a priori impossible, is extremely improbable. We should then necessarily find discontinuous regions corresponding to transition to the $^1\Sigma$-curve of the ionic binding and also further discontinuous transitions to atomic binding curves, leading in the limit to excited atoms.† Such regions of absorption have not been observed, although Schmidt-Ott has pushed his investigations into the Schumann region. Finally, the observed course of the fundamental vibration quanta would have to be continued in another way in order to lead to the limit corresponding to two normal atoms. The fact, however, that a continuous region of absorption, leading to normal atoms, has alone been observed

* H. D. Schmidt-Ott, *Zeitschr. f. Physik*, 69, 724 (1921).

† The transition from atomic binding as fundamental state to ionic binding as excited state must give rise to a discontinuous region, as in theory the ionic binding cannot have very flat potential curves. Other discontinuous regions should arise, for if the atomic binding curve of the fundamental state has a deep minimum, the occurrence of atomic binding curves of excited states with well-marked minima is also to be expected.

TABLE I

	Position of Maxima (Exp.) in Å	Classification	Observer *	$\Delta\nu_1$ for the Maxima (Exp.)		$\Delta\nu_2$ Atomic Term Differences	
			CsI				
					Cm.$^{-1}$		Cm^{-1}
1	3240	Cs (1S)+I ($^2P_2$)	F.	1–2	7,900	I ($^2P_2$ — $^2P_1$)	7,600
2	2580	Cs (1S)+I ($^2P_1$)	recent	1–3	10,900	Cs (1S—2P_1, 2P_2)	11,450
3	2395	Cs (2P_1, 2P_2)+I ($^2P_2$)	recent	1–4	16,200	Cs (1S—3D_1, 3D_2)	14,550
4	2125	Cs (3D_1, 3D_2)+I ($^2P_2$)	recent	1–5	19,400	Cs (1S—2S)	18,550
5	1990	Cs (2S)+I ($^2P_2$)	recent	1–6	23,200	Cs (1S—3P_1, 3P_2)	21,850
6	1850	Cs (3P_1, 3P_2)+I ($^2P_2$)	recent				
			CsBr				
1	2750	Cs (1S)+Br ($^2P_2$)	M.	1–2	3,000	Br ($^2P_2$—$^2P_1$)	3,700
2	2540	Cs (1S)+Br ($^2P_1$)	M.				
			CsCl				
1, 2	2470	Cs (1S)+Cl ($^2P_2$, $^2P_1$)	M.	1–3	11,000	Cs (1S—2P_1, 2P_2)	11,450
3, 4	1940	Cs (2P)+Cl ($^2P_2$, $^2P_1$)	recent				
			RbI				
1	3240	Rb (1S)+I ($^2P_2$)	M.	1–2	8,000	I ($^2P_2$—$^2P_1$)	7,600
2	2580	Rb (1S)+I ($^2P_1$)	recent	1–3	11,200	Rb (1S—2P_1, 2P_2)	12,700
3	2380	Rb (2P_1, 2P_2)+I ($^2P_2$)	recent				
			NaI				
1	3240	Na (1S)+I ($^2P_2$)	M.F.	1–2	8,000	I ($^2P_2$—$^2P_1$)	7,600
2	2580	Na (1S)+I ($^2P_1$)	F.	1–3	16,300	Na (1S—2P_1, 2P_2)	16,950
3	2120	Na (2P_1, 2P_2)+I ($^2P_2$)	recent				

* F ≡ J. Franck, H. Kuhn, and G. Rollefson, *Zeitschr. f. Physik*, **43**, 155 (1927): M ≡ L. A. Müller, *Ann. d. Physik*, **82**, 39 (1927).

is no objection to the conception adopted here—$^1\Sigma$-curve in the fundamental state with dissociation into ions and $^1\Sigma$-curve or $^1\Pi$-curve in the excited state with dissociation into normal atoms. If all the atomic binding curves are very flat, the differences between the $^1\Sigma$- and $^1\Pi$-curves must be small, and hence they will give rise to a common continuous region.

From the experimental point of view, therefore, the intersection of the curves is very much more probable and a unique classification is possible. Such cases have been dealt with theoretically by von Neumann and Wigner,* and also by Weizel † and London.‡ According to them the probability of the curves crossing or avoiding one another depends on the sharpness with which the quantum properties are defined and on the velocity with which the point of intersection is traversed. For the alkali halides in particular, as London points out, the point of intersection corresponds to a fairly large internuclear distance, and would have to be traversed extremely slowly for the curves to avoid one another, and this is not the case. Clearly, then, the experimental and theoretical results are in agreement.

(*b*) *Atomic Molecules.*

The characteristic features of ionic molecules are, as we have seen, dissociation from the fundamental state into oppositely charged ions and dissociation from the first stage of dissociation, which may be brought about by light, into normal atoms. For atomic molecules the convergence of the vibrational quanta of the fundamental state gives decomposition into atoms. As a rule these are normal atoms. The first state of excitation usually gives rise to one normal atom and one excited atom. Exceptions may occur, however. For example, it is possible for the most stable state of a molecule to arise from the combination of a normal atom and an excited atom, and for the excited state to lead in the limit to normal atoms. § (We therefore may not draw the converse conclusion that every molecule which is dissociated into two normal atoms on absorption of light is an ionic molecule.) Further, the fundamental state and the excited state lead to normal atoms. For example,

* J. von Neumann and E. Wigner, *Phys. Zeitschr.*, 30, 467 (1929).

† W. Weizel, *Zeitschr. f. Physik*, 59, 320 (1930).

‡ F. London, *Zeitschr. f. Physik*, 46, 455 (1928).

§ G. Herzberg, *Ann. d. Physik* (4), 86, 189 (1928)

the following shape of the potential curves for N_2^+,* CN, and SiN† is probable, although not absolutely certain ‡ (fig. 6).

From this we may conclude that the first states of excitation of these molecules give dissociation into normal atoms. From the purely experimental side, however, we cannot say what products arise from the fundamental state, in view of the magnitude of the extrapolation and our unsatisfactory knowledge of the lower terms of N_1^+, C, and Si. Experimentally we can only infer that they are probably excitations of N^+, C, and Si, as if N were excited the energies of excitation would necessarily always be the same. Heitler and Herzberg thought that the ^5S term must be taken as a stage of excitation. In this term the carbon atom would according to the Heitler-London valency theory be tetravalent, while in the fundamental term ^3P it must appear as divalent. This would mean that the carbon atom requires excitation before its valency is fully activated. According to the most recent results by Hund,§ however, these considerations are to be rejected, so that the final interpretation of the dissociation products in the cases named, by either experimental or theoretical means, is still awanting. For the point of intersection the same considerations apply as before.

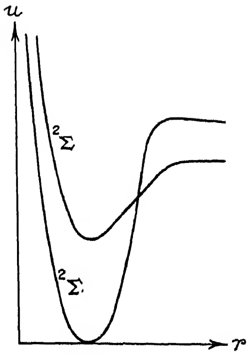


Fig. 6

Although it has always been possible hitherto to distinguish experimentally between atomic molecules and ionic molecules, we of course have theoretically to consider the possibility of the discovery of an intermediate case in which definite classification is not possible. Even when convergence of the bands is observed, the classification of the products of dissociation is by no means always easy. This is often due to the fact that the atomic spectra

* G. Herzberg, *Ann. d. Physik* (4), **86**, 189 (1928).

† W. Heitler and G. Herzberg, *Zeitschr. f. Physik*, **53**, 58 (1929).

‡ According to a remark made by Herzberg during the discussion, Birge (in a written communication to the former) considers that another extrapolation for the vibrational quanta of the excited state $^2\Sigma$ of CN is possible. It can scarcely lead to the same limit as the fundamental state, as two $^2\Sigma$-terms cannot arise from normal C and N. Birge also considers it possible that the excited state goes to a higher limit than the fundamental state. In Herzberg's extrapolation the deviations from a smooth curve obtained by Birge would be regarded as perturbations.

§ Mentioned in a lecture delivered in Göttingen in June, 1931.

are not accurately known (see above, CN and N^+). Thus, for example, the energy of dissociation of O_2 has only recently been found accurately. The uncertainty is often due to the small magnitude of the energy of excitation. For example, there are available all sorts of experimental data relating to the problem whether the first excited state of ICl dissociates into I ($^2P_{3/2}$) and Cl ($^2P_{1/2}$) or into two normal atoms.* For reasons of analogy with the halogens I

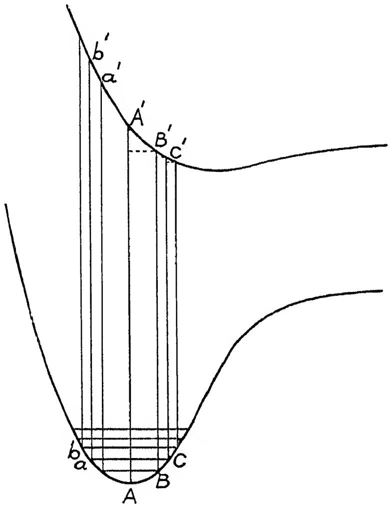


Fig. 7

have adopted the former view. Mulliken † has now attempted to clear up the matter from the theoretical point of view, and has interpreted the visible ICl bands as the transition $^1\Sigma^+—^3\Pi_0$. He accordingly considers it more probable that the excited state, like the fundamental state, dissociates into two normal atoms. It has however, recently been discovered by Cordes ‡ that the corresponding system of bands of IBr in the limit gives one excited atom and one normal atom.

If there are no sharp-headed bands, but merely blurred-looking

* G. E. Gibson and H. C. Ramsperger, *Phys. Rev.*, **30**, 598 (1927); E. D. Wilson, *Phys. Rev.*, **32**, 611 (1928); G. E. Gibson, *Zeitschr. f. Physik*, **50**, 692 (1928); J. Patkowski and W. E. Curtis, *Trans. Farad. Soc.*, **25**, 725 (1929); W. E. Curtis and O. Darbyshire, *Trans. Farad. Soc.*, **27**, 77 (1931); G. K. Rollefson and F. C. Lindquist, *J. Amer. Chem. Soc.*, **52**, 2793 (1930); **53**, 1184 (1931).

† R. S. Mulliken, *Phys. Rev.*, **37**, 1412 (1931).

‡ H. Cordes, *Zeitschr. f. Physik*, **74**, 34 (1932).

bands, there may again be fluctuations of intensity* such as we discussed above. In fig. 7 the regions of transition which are associated with the points of reversal of the vibration B, C, &c., are separated from one another owing to the flatness of the upper curve, and in the region of large internuclear distance the distances between them are given by the magnitude of the fundamental vibrational quanta. For small internuclear distances, say A′, however, the upper curve is much steeper. Hence the distances between the maxima are at first much greater than the fundamental vibrational quanta, and then decrease more rapidly than these. These pseudo-convergences, which give the effect of blurred bands, may easily lead us to false conclusions. The erroneous values for energies of dissociation obtained by Mrozowski † and Jablonski,‡ for Hg_2, Cd_2, and Zn_2, are partially based on such evidence.

(*c*) *Van der Waals Molecules.*

Hitherto we have met with no cases in which the binding is extremely loose in the *fundamental state*. Such examples, however, are known; to this type belong e.g. the molecules of the metallic vapours Hg, Cd, Zn. The experimenter infers their existence from the following spectroscopic behaviour. As an example we shall take Hg. At low pressures mercury vapour exhibits only the atomic lines in absorption. At higher pressures broad absorption bands appear in association with the atomic lines. Under certain conditions it has been found possible to detect structure in these bands in emission or absorption (Lord Rayleigh,§ Steubing,|| and others), whence Kuhn¶ was able to deduce e.g. the magnitude of the fundamental vibrational quanta (20 cm.$^{-1}$). The shading-off of the absorption bands on the short-wave side shows that the potential minimum of the fundamental state corresponds to a greater internuclear distance than that of the excited state. On the short-wave side the bands give way to apparently continuous fluctuations of intensity, the breadths and distances between which diminish with the wave-length. The intensity fluctuations are of the kind we

* H. Kuhn, *Zeitschr. f. Physik*, **63**, 458 (1930).

† S. Mrozowski, *Zeitschr. f. Physik*, **50**, 657 (1928); **55**, 338 (1929); **62**, 314 (1930).

‡ A. Jablonski, *Bull. de l'Acad. Pol.* (1928), p. 163.

§ Lord Rayleigh, *Proc. Roy. Soc.*, A, **116**, 702 (1927).

|| W. Steubing, *Phys. Zeitschr.*, **10**, 787 (1909).

¶ H. Kuhn, *Naturwiss.*, **16**, 352 (1928).

discussed, except that the fundamental state is now the state of loose binding and the excited state that of rigid binding. The behaviour of Cd and Zn is similar, as has been shown by Winans;* it is illustrated in fig. 8.

The distance between the horizontal parts of the curves corresponds to the $h\nu$ of the atomic line 2288 Å. Transitions from the flat minimum of the loose fundamental state, i.e. from *c* to the potential curve of the higher state, give the slight broadening of the line on the short-wave side, ending in a sharp band-head. As the internuclear distance diminishes so does the vertical distance between the curves. The decrease is particularly rapid where the

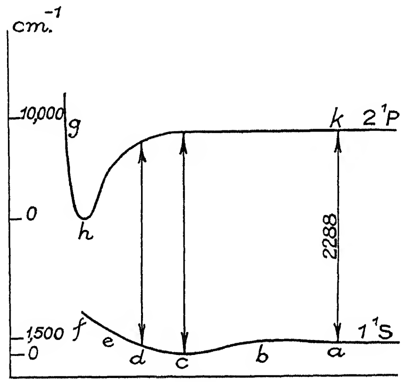


Fig. 8

upper curve falls steeply to its minimum. This explains the broadening on the long-wave side, which rapidly increases with rising pressure and particularly with rising temperature, as an increase of temperature makes the amplitudes of vibration greater and enables the atoms to approach one another more closely. The extremely small energy of dissociation of these metallic molecules suggested that no real chemical binding is to be assumed here. For Hg, as was deduced from the strength of the absorption band 2540 Å. at differing temperatures and pressures, it is of the order of 1 kilocalorie.† It was assumed that the binding in the fundamental state is of the type of the general van der Waals attraction. In the excited states ordinary rigid binding may occur. It must be emphasized that on the experimental side we have no criterion of the occurrence

* J. G. Winans, *Phil. Mag.*, 7, 555 (1929).

† E. Koernicke, *Zeitschr. f. Physik*, **33**, 219 (1925).

of this loose binding in the fundamental state apart from the discovery of particularly small energies of dissociation in the fundamental state and the established fact that the diffuse bands which occur are associated with the atomic lines of the element in question, while in the molecules with genuine binding the position of the transitions between the potential curves has nothing to do with the position of the atomic lines. We accordingly have no dis-

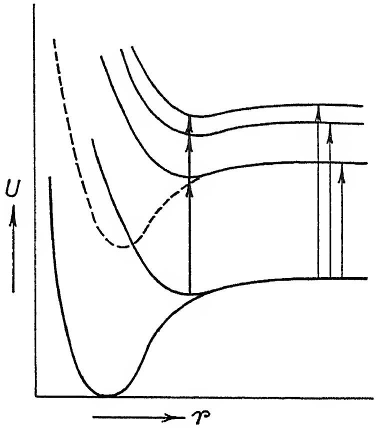


Fig. 9

tinguishing criteria such as are available for atomic molecules and ionic molecules. It is particularly satisfactory that the existence of these van der Waals molecules in potassium vapour also has been established by Kuhn.* The relationships are illustrated in fig. 9.

In the fundamental state there is a repulsion curve with a very flat minimum of potential, as well as an attraction curve. From the appearance and behaviour of the bands, which occur on the short-wave side of a number of lines (e.g. 3035 Å., 1S–7P, 2992 Å., 1S–8P), Kuhn also infers the existence of a loose excited state. The bands arise from transitions between these terms. The existence of a loosely bound molecule of this type is intelligible from the theoretical point of view. Just as in the case of hydrogen, the approach of two K atoms, owing to exchange forces, does not invariably lead to attraction, giving the well-known K_2 molecule; with a different orientation of the spin vectors repulsion may follow. This continually falling potential curve must combine with the attraction

* H. Kuhn, *Naturwiss.*, 18, 332 (1930).

potential of the van der Waals forces (as these decrease more slowly with distance) so as to give a potential minimum, as was theoretically calculated for H_2 by London and Eisenschitz.* The molecules HgA and HgKr discovered by Oldenberg † are of the same type.

The phenomena of light absorption by gaseous, liquid, and solid xenon, recently described by McLennan and Turnbull, ‡ are explained by Franck § in a way analogous to Winans' explanation of the absorption in Cd and Zn vapour. With increasing pressure the xenon resonance line at 1469 Å. behaves in the same way as that of mercury. In the passage to the liquid state the long-wave boundary is displaced from the original line by several hundred Ångstrom units. This is explained by the great diminution of the internuclear distances in the liquid state. If, further, we observe the absorption of solid xenon, the region of absorption again becomes narrower as the temperature falls. The broadening on the short-wave side is slight and reaches a limiting value as the pressure is raised. As in the case of Hg_2, the narrowing of the spectrum is due to the fact that in spite of increasing density the atoms cannot approach one another so closely owing to the diminution of the amplitudes of vibration. (Larger aggregates of molecules may, of course, be present.)

According to the principles developed above, the alkali halides in the vapour form are ionic molecules, while the halides of thallium and silver and the halogen acids are polar atomic molecules. As was said before, no difficulties have hitherto arisen in the classification. In many cases it is possible to make exact statements as to the correlation of the various atomic states with the molecular states. Particularly loose molecular states can also be recognized from their spectroscopic behaviour. There is, however, a group of molecules for which it is impossible to decide definitely whether they should be reckoned as atomic molecules or as molecules with loose van der Waals binding. These are the hydrides and halides of the elements in the second column of the periodic table. The hydrides, which have been chiefly investigated by Hulthén and his fellow-workers, would according to the spectral evidence have to be reckoned as atomic compounds. The spectra are comparatively well known, even the correlation of the various atomic terms with

* Eisenschitz and F. London, *Zeitschr. f. Physik*, **60**, 491 (1930).

† O. Oldenberg, *Zeitschr. f. Physik*, **55**, 1 (1929).

‡ J. C. McLennan and Turnbull, *Proc. Roy. Soc.*, A, **129**, 266 (1930).

§ J. Franck, *Naturwiss.*, **19**, 217 (1931).

the molecular terms being known. In all cases the binding is looser in the fundamental state than in the excited state. According to the valency theory of London and Heitler, the assumption of genuine homopolar binding in the fundamental state would make difficulties, as the latter arises from a metallic atom in the ^1S-state. Opinion has therefore tended rather to the assumption that the binding is of the van der Waals type. In actual fact the energy of dissociation of HgH is only 0·4 volt.* The other hydrides, however, exhibit rapidly increasing binding energies: CdH $\sim$ 0·7; ZnH $\sim$ 0·9; CaH $\sim$ 0·6; MgH $\sim$ 0·7; BeH $>$ 1 volt, probably as much as 2 volts. These are of a different order of magnitude from the binding energies of the van der Waals molecules discussed above. The relationships are still more extreme in the case of the halides of the same column.† Here in analogy with the hydrides we may expect the nature of the binding to be the same. The energies of dissociation vary between 1 and 2 volts, i.e. are of the order of magnitude obtained for genuine binding. The ideas recently developed by Hund may perhaps enable us to explain these cases.‡

Dissociation by Rotation

In conclusion, a few remarks may be devoted to the dissociation process which may arise from an increase of the rotational energy (with an electronic jump). A molecule can in itself take up as rotational energy an amount of energy exceeding the energy of dissociation of the state in which it is. The final decomposition may arise from two causes: rotation may give rise to mechanical instability or decomposition by predissociation may occur.

Oldenberg § has given a strict criterion for the occurrence of mechanical instability when the rotations are large and the energy of dissociation small, and has applied it to mercury hydride. The bands corresponding to transitions from higher electronic states to the fundamental state all break off for a definite rotational quantum (different for the different vibrations) of the lower state. These rotational levels all lie much higher than the energy of dissociation of the state. Oldenberg's considerations are briefly as follows: for the rotating molecule (vibration being neglected) the

* E. Hulthén, *Zeitschr. f. Physik*, **32**, 32 (1925).

† H. Sponer, *Zeitschr. f. Phys. Chemie* (B), **11**, 425 (1931).

‡ See F. London, *Zeitschr. f. Physik*, **63**, 245 (1930); *Zeitschr. f. Phys. Chemie*, B, **11**, 222 (1930).

§ O. Oldenberg, *Zeitschr. f. Physik*, **56**, 563 (1929).

equilibrium distance is determined by the condition that the centrifugal force must be equal to the force of attraction, i.e. $p^2/\mu r^3 = U_0'(r)$, where p is the angular momentum, μ the reduced mass, r the internuclear distance, and $U_0'(r)$ the derivative of the potential energy for zero rotation. If we superpose a vibration on this state of equilibrium, the restoring force is $p^2/\mu r^3 - U_0'(r)$. This force may be represented as the differential coefficient of the curve

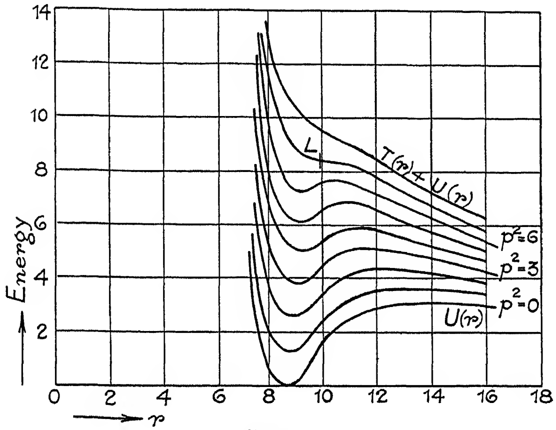


Fig. 10

$- p^2/2\mu r^2 - U_0(r)$. This curve (regarded as a function of r) has a simple physical meaning. The differential coefficient gives the force, the position of the minimum the position of equilibrium, and the depth of the minimum the stability of the rotating molecule. That is, for the rotating state the curve has the same meaning as the potential curve $U_0(r)$ has for the non-rotating state. The quantity $p^2/2\mu r^2$ is simply the kinetic energy of the rotation. Fig. 10 gives the family of curves $U(r)$ obtained in this way by Oldenberg for various values of p, on an arbitrary scale. For large values of r all the curves approach the same value asymptotically, the value corresponding to the limit of dissociation of the state. (For if the internuclear distance is large, states with differing angular momenta cannot differ greatly.) Starting from large values of r the $U(r)$ curves pass through a maximum * for $p > 0$, and only subsequently through the minimum

* If the potential energy $U_0(r)$ contains no higher power of $1/r$ than $1/r^2$, this maximum does not occur. This, however, only happens in ionic molecules in which the rotational energy does not exceed the energy of dissociation even if decomposition occurs. The cases which have actually been observed involve atomic molecules only.

which corresponds to the position of equilibrium, while the curves $U_0(r)$ do not possess a maximum of this type. As p increases, the minimum flattens out and finally coincides with the maximum, forming the point of inflexion L. For still higher rotational states the molecule becomes mechanically unstable. This occurs for a value of the rotational energy (see fig. 9) which is decidedly greater than the energy of dissociation. That the rotational states below this limit are mechanically stable, even if they lie higher than the dissociation limit, is due to the fact that they are separated from the dissociated state by a maximum of potential.

If there is a transition from any of the other states into one of the unstable rotational states the molecule decomposes. As in these states r is only slightly increased, the energy of the molecule is composed of a small amount of pure potential energy $U_0(r)$ and a large amount of rotational energy $p^2/2\mu r^2$. The decomposition occurs with conservation of angular momentum, i.e. on the curve $T(r) + U(r)$. If r is large, $U(r)$ finally becomes $U_0(r)$. In the decomposition the energy is transformed into energy of dissociation and kinetic energy of translation.

Oldenberg calculated the $U(r)$ curves for the fundamental state of mercury hydride, and found that the rotational quantum $J = 31$ lies slightly below the point where instability sets in. The breaking-off of the bands is actually observed in this rotational state. As in addition to the rotation there is still the zero-point vibration of 0·085 volt, the agreement is good. If higher vibrational quanta are added we may expect to find the bands breaking off at lower rotational states, since the minima of the last few curves before instability is reached are very flat; and this, in fact, is actually observed. From the curves we also see that with increased rotation the internuclear distance for the position of equilibrium is only slightly altered (by 11 per cent for HgH, in agreement with the value of 9 per cent found experimentally).

The last few rotational states before the limiting curve are broadened. The explanation of this is based on quantum mechanics. According to the principles of quantum mechanics the probability of a transition occurring between two states of equal energy separated by a maximum of potential is finite, the transition, according to Kronig,* being subject to certain selection rules. Franck's principle, however, must also be fulfilled, and attempts †

* See the following paper by Kronig (p. 143).

† J. Franck and H. Sponer, *Gött. Nachr.*, p. 241 (1928).

were made to explain the instability of rotation in HgH and AlH by a quantum-mechanical "breach effect" like this, retaining Franck's principle. It was then established by Oldenberg that the sudden breaking-off of the bands is explained by mechanical instability alone, at least in the case of HgH. It is only the blurring of the last few rotational states, which was investigated more carefully for HgH by Kapuscinski and Eymers,* that depends on the quantum-mechanical "breach effect". Oldenberg's explanation is also applicable to CdH and ZnH and perhaps also, as will be discussed by Kronig (p. 152), to the $^1\Pi$-term of AlH. A more accurate theoretical representation of these relationships on the basis of the quantum mechanics has since been given by Kronig,† Condon and Villars,‡ and Rice.|| The occurrence of dissociation phenomena arising from the intersection of two potential curves is discussed in detail by Kronig in the next paper but one (p. 143).

* W. Kapuscinski and J. G. Eymers, *Zeitschr. f. Physik*, **54**, 246 (1929).

† R. de L. Kronig, *Zeitschr. f. Physik*, **62**, 300 (1930).

‡ D. S. Villars and E. U. Condon, *Phys. Rev.*, **35**, 1028 (1930).

|| O. K. Rice, *Phys. Rev.*, **35**, 1538, 1551 (1930).

The Experimental Basis of the Theory of Predissociation of Molecules

VICTOR HENRI, MARSEILLES

In the year 1923 I drew attention * to the fact that in a large number of cases the absorption spectrum of a vapour consists of narrow bands which are entirely continuous; in these cases, therefore, the vibrations of the atoms are probably quantized, whereas the rotation of the molecules is not.

Investigation of the absorption spectra of a number of molecules both simple and complicated (S_2, SO_2, CS_2, NO_2, NH_3, CH_3NH_2, CH_3COH, HCOH, Cl_2CO, $H_2C:C:O$, HCOCOH, pyrrole, furane, furfuraldehyde, pyridine, benzene derivatives, naphthalene, &c.) showed that for one and the same substance the absorption spectrum with fine structure (rotational quantization) passes with shorter wave-lengths into a blurred one consisting of diffuse bands.†

The state of the molecule in which the bands are diffuse I call *predissociation*, because it has been found that in this state the molecules are chemically very reactive. At the same time as Born and Franck ‡ I ascribed the vanishing of the rotational quantization to the very brief duration (about 10^{-12} sec.) of the predissociation state of the molecule and indicated even at that time that there is a connexion between the limit of predissociation and the strength of binding of the atoms in the molecule.

The scope of the investigations and the theoretical interpretation of predissociation were greatly developed in the following years. It is now generally recognized that in this state the molecules are

* *Comptes Rendus*, **177**, 1037 (1923).

† The first papers we published on this subject are as follows: V. Henri and H. de Lazlo, *Proc. Roy. Soc.*, A, **105**, 662 (1924); V. Henri and Teves, *Comptes Rendus*, **179**, 1156 (1924); *Nature*, **114**, 894 (1924); V. Henri, *Structure des molécules*, pp. 82–103 (Paris, 1925).

‡ *Zeitschr. f. Physik*, **31**, 411 (1925).

very active, that their life is very short, and that the predissociation limit gives an *upper* limit for the energy of dissociation.

Here I should like to state some new facts recently established by myself and my fellow-workers, which show that the phenomena of predissociation extend still farther.

1. *Acetaldehyde.*—Acetaldehyde is quantitatively decomposed into carbon monoxide and methane by ultra-violet irradiation:

$$CH_3COH \rightarrow CO + CH_4.$$

In collaboration with J. H. C. Smith we have quantitatively investigated this reaction in the vapour state, various types of radiation being used. Acetaldehyde at a pressure of between 60 and 630 mm. was introduced into a quartz tube with plane glass windows fused on. The tube was 10 cm. long and had a diameter of 1·3 cm. It was illuminated by parallel rays from a very strong mercury-vapour lamp. The rays were separated into various groups by means of a number of filters (glass, mica, vita-glass, 1 cm. 5 per cent benzene, 25 cm. chlorine at a pressure of 600 mm., 1 cm. 0·028 and 0·05 molar solutions of crotonic acid). The energy of the incident and absorbed light was determined by a thermopile and expressed in calories by comparison with a Hefner lamp.

The irradiation vessel was connected with a manometer so that the change in pressure could be followed out. At the close of the experiment the gases were removed and analysed by means of a micro-burette using Christiansen's method.* As 1 mm. of the capillary of our burette corresponded to a volume of 0·35 mm.^{3}, the gas analysis could be carried out correct to 2 per cent with a total volume of 20 mm.^{3}

It was found that at room temperature the rays of wave-length exceeding 3050 Å. produced no dissociation of acetaldehyde in spite of very prolonged irradiation. For shorter wave-lengths the reaction goes as follows:

0·0015	mm.^{3} CO	per minute	between	3050	and	2950 Å.
0·0146	,,	,,	,,	2950	,,	2870
0·0341	,,	,,	,,	2870	,,	2770
0·0417	,,	,,	,,	2770	,,	2450
0·0350	,,	,,	,,	2725	,,	2450

These numbers are for a pressure of 170 mm. ($c = 1/100$ molar) and a body of gas 10 cm. thick.

* *Journ. Amer. Chem. Soc.*, **47**, 109 (1925).

The molecular extinction coefficient ϵ (defined by $I_1 = I_0 \cdot 10^{-\epsilon c d}$) was measured by means of a thermopile and also by the photographic method; the results are given in the following table. The third column gives the percentage absorbed by the vapour under the same conditions.

TABLE I

λ	ϵ	% absorbed.	$c = N/100$, $d = 10$ cm.
3306	2·31	41	
3259	3· 3	54	no reaction
3220	5·39	71	
3100	9·01	87	
3002	15·89	97	activity 15
2926	19·26	98·8	,, 146
2813	19·26	98·8	,, 341
2765	15·89	97	
2628	10·96	92	
2550	5·39	71	,, 417
2450	2·89	48	

The absorption spectrum of acetaldehyde vapour was investigated by us in collaboration with S. A. Schou.* It consists of a large number of sharp bands with beautiful rotational structure between $\lambda = 3484$ and $\lambda = 3050$. In the neighbourhood of 3050 the bands then become blurred fairly rapidly (predissociation) and about 60 of these diffuse bands can be measured, reaching to 2823 Å. At the same time there is superposed on them a broad continuous band starting at about 3080 Å. and having a maximum at 2850 and subsequently falling away more and more on the ultra-violet side.

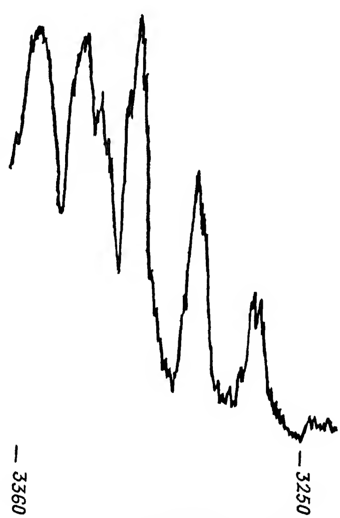


Fig. 1.—Acetaldehyde, normal

Thus we see that the photochemical action coincides with the beginning of predissociation.

In figs. 1 and 2 we give the microphotographs of a part of the spectrum with rotation structure between 3360 and 3250 Å. and a part (3060 to 2985) of the predissociated spectrum.

* *Journ. de Chim. Phys.*, 27, 27 (1929).

If we now heat the acetaldehyde vapour to 200° C. and photograph the spectrum, we merely obtain quite feeble diffuse bands between 3500 and 3200 Å. and strong continuous absorption reaching far into the ultra-violet. Irradiation of the vapour at this temperature shows that even rays of wave-length exceeding 3100 can now give rise to dissociation into CO and CH_4.

Rise of temperature alone can bring about this dissociation also, but only above 430°, as has been shown by Hinshelwood and Hutchinson.* These workers showed that the thermal reaction is bimolecular, has a heat of activation of 45,500 calories, and is represented very closely by the number of active collisions.

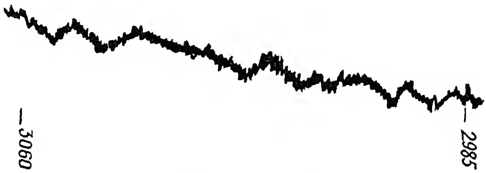


Fig. 2.—Acetaldehyde, predissociated

2. *Benzaldehyde.*—The behaviour of benzaldehyde is quite analogous to that of acetaldehyde; under the action of ultra-violet radiation it decomposes into benzene and carbon monoxide:

$$C_6H_5COH = C_6H_6 + CO.$$

The photochemical reaction in the vapour state has been investigated quantitatively by myself in collaboration with M. de Hemptinne † and later with F. Almasy.‡ The absorption spectrum has been analysed by Almasy.

The spectrum consists of three regions:

1. Between 3747·3 and 3162·6, 159 bands with sharp heads have been measured; these are obtained with a concentration of 40 mg. per litre when $d = 100$ cm.

2. Between 2963·0 and 2599·2 there are 51 bands, which are also very sharp. These bands are obtained with a concentration of 1 mg. per litre.

3. Between 2428 and 2349 there are 6 diffuse bands of breadth about 80 cm.$^{-1}$. These bands are observed with a concentration of 0·05 mg. per litre when $d = 100$ cm.

If the temperature is raised to 200°, the bands of the second

* *Proc. Roy. Soc.*, A, **111**, 380 (1926).

† *Journ. de Phys. et Rad.*, **9**, 357 (1928). ‡ Work not yet published.

region are entirely blurred, and a region of continuous absorption is superposed on them. We see only the bands of the first series to 2840 and very feebly to 2810, the other bands no longer appearing. Fig. 3 (Plate IV) gives a part of the absorption spectrum of benzaldehyde at 20° and at 200° C. This was obtained by introducing benzaldehyde vapour at a pressure of 0·2 mm. at 20° C. into a quartz tube 30 cm. long; the tube was then closed (after the benzaldehyde had been condensed in a side-tube by means of liquid air) and the spectrum photographed at various temperatures. The tube was then irradiated with light of various wave-lengths, and the spectrum again photographed. If photochemical decomposition occurs, the benzene bands are shown; the sensitivity is so great that dissociation amounting to only 1–2 per cent is easily detected. At the close of the experiment the gas in the tube was transferred to a McLeod gauge, the volume determined, and the gas then analysed by a micro-burette. A gas analysis could be carried out with a volume as low as 2 $mm.^3$

At 20° C. the rays between 2600 and 2405 Å. (Cl_2 filter + crotonic acid filter) give rise to strong dissociation, which is almost complete in 2–3 hr. We thus obtain about 98 per cent CO, together with benzene and some hydrogen.

The rays of wave-length exceeding 2700 Å. (benzene filter) give rise to no reaction at 20° in spite of an exposure lasting 16 hr.

At 200° the same rays ($\lambda > 2700$ Å.) give rise to strong dissociation. If at this temperature we interpolate a glass filter which cuts out all rays of wave-length exceeding 3214, no reaction follows even with 65 hr. exposure. At this temperature the bands of the first region (3747 to 3162) are still quite sharp.

If the temperature is raised to 250° the bands of the first region (3747 to 3162) also become blurred and a strong continuous absorption is superposed on them; irradiation with wave-lengths exceeding 3214 Å. at this temperature gives rise to marked dissociation into C_6H_6 and CO.

Heating without irradiation does not give rise to appreciable decomposition until temperatures of 400°–500° are reached.

The mechanism of the reaction is probably given by

$$C_6H_5COH \rightarrow C_6H_5 + COH,$$

the products then chiefly decomposing into C_6H_6 and CO, although small proportions of $C_6H_5 . C_6H_5$, H_2, CO, or glyoxal (HCO . COH)

may also be formed. The formation of a small quantity of hydrogen would thus be explained. The presence of diphenyl and glyoxal could not be established spectroscopically, but the sensitiveness of the diphenyl and glyoxal bands is not very great.

3. *Formaldehyde.*—In collaboration with S. A. Schou I have investigated the spectrum of formaldehyde.* It consists of bands between 3570 and 2500 Å. The bands above 2750 exhibit a very beautiful doubled rotation structure, which corresponds to rotations about the symmetrical CO axis (smaller moment of inertia $I_0 = 1{\cdot}38 \,.\, 10^{-40}$) and an axis perpendicular to it (greater moment of inertia $K_0 = 50 \,.\, 10^{-40}$).

In the band H ($\lambda = 2750$) the fine structure of the second very fine rotation is no longer to be seen; there remain only the lines of the first rotation, which are somewhat broadened. In the next band K ($\lambda = 2670$) even the lines of the first rotation are quite blurred. The remaining ultra-violet bands are quite continuous, with a breadth of 10–20 Å.

The limit of predissociation is not very sharp; a gradual transition extending over about 70 Å. takes place. In fig. 4 (Plate IV) we give the photographs of three bands:

(1) between $\lambda = 3160$ and 3130 with double rotation;
(2) from 2720 to 2700 with only one rotation;
(3) from 2680 to 2660 with diffuse bands.

If the temperature is raised to 220° the limit of predissociation is displaced towards the visible region.

The photochemical decomposition of formaldehyde has been investigated by Kirkbride and Norrish.† On irradiating formaldehyde vapour with rays of wave-length between 2800 and 2650 Å. they obtained a quantitative dissociation into CO and H_2. That is, the reaction

$$\begin{matrix} H \\ H \end{matrix}\!\!>\!C = O \;\rightarrow\; H_2 + CO$$

is set up by the radiation of the region of predissociation.

The primary reaction is certainly the splitting-off of hydrogen, i.e.

$$H_2CO \;\rightarrow\; H + HCO,$$

analogously to the phenomena of the dissociation of phosgene,

* *Zeitschr. f. Physik*, **49**, 774 (1928).
† *Trans. Farad. Soc.*, **27**, 404 (1931).

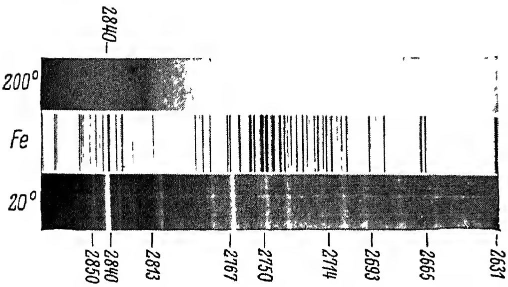


Fig 3.—Benzaldehyde at 20° C. and 200° C

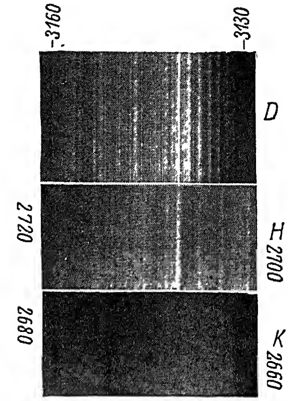


Fig. 4 —Formaldehyde

D (3160–3130) double rotation
H (2720–2700) single rotation
K (2680–2660) predissociated

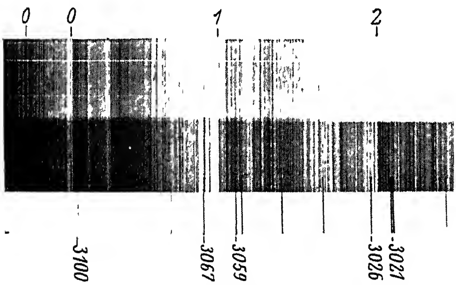


Fig. 8.—Sulphur (S_2) Spectrum, normal

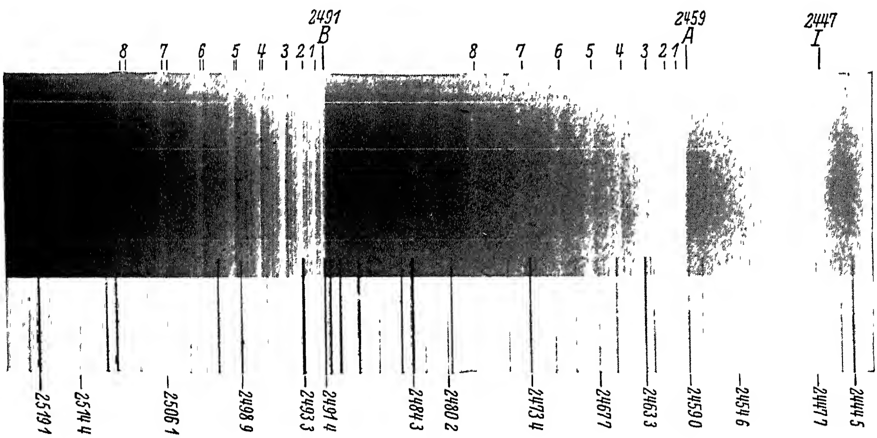


Fig. 5.—Sulphur Dioxide Bands B, A, and I (predissociated)

where according to Bodenstein * the reaction first takes place according to the equation

$$Cl_2CO \rightarrow Cl + ClCO.$$

The limit of predissociation gives the upper limit of the energy of dissociation; for the binding energy of a hydrogen atom in formaldehyde we therefore have

$$D \leq 105 \text{ Cal. } (2750 \text{ Å.}).$$

The vibration spectrum of formaldehyde was first analysed by us and then more completely by Herzberg.† One of the two fundamental vibrations (1572 cm.$^{-1}$) of the normal molecule corresponds to the vibration $C \longleftrightarrow O$; from the convergence Herzberg obtains the energy 195 Cal. for the dissociation of H_2CO into H_2C+O. As thermochemical data lead to the value 155 Cal. for this reaction, we infer that dissociation brings about the formation of excited oxygen by increasing the vibrational quanta, the oxygen being in the ^1D-state, which requires 45 Cal. for its excitation.

The point of convergence for the dissociation

$$H_2CO \rightarrow H_2C + O^*(^1D)$$

is 69,000 cm.$^{-1}$ or $\lambda = 1449$ Å., according to Herzberg; here, then, there should be a second limit of predissociation. This has not yet been observed, but a second range of absorption bands has been discovered in formaldehyde vapour below 1560 Å.

4. *Ammonia.*—The photochemical decomposition of ammonia by monochromatic light was first investigated by E. Warburg,‡ and subsequently by W. Kuhn § in my laboratories; I have recently reinvestigated the question.

At ordinary temperatures it is found that only rays of wavelength below 2140 (Zn lines 2025, 2062, 2100, 2139) give rise to dissociation. The Cd lines (2329, 2321, 2313, 2307, 2288, 2265, and 2195) have no effect.

At 20° C. a molecule of NH_3 is dissociated on absorption of from 2·5 $h\nu$ (Kuhn) to $4h\nu$ (Warburg).

The absorption spectrum consists of a number of double bands ($\Delta\lambda = 6 - 8$ Å.) occurring at regular intervals of about 40 Å. between

* *Zeitschr. f. phys. Chemie*, B, **3**, 459 (1929).

† *Trans. Farad. Soc.*, **27**, 378 (1931).

‡ *Sitzb. d. Akad. Berl.* (1911, 1912).

§ *Journ. de Chim. phys.*, **23**, 521 (1926).

2360 and 1935 Å. The first few bands, 2360–52, 2321–12, 2283–75, 2243–35, and 2213–07, are sharp and even exhibit rotation structure. The bands farther in the ultra-violet, 2167–60, 2127–20, 2089–83, 2048, 2005, 1975, and 1935, on the other hand, are diffuse and the blurring steadily increases towards the ultra-violet. This spectrum has also been studied by Ferrières.*

We see then that the photochemical effect coincides with the onset of predissociation (Bonhoeffer and Farkas).

The effect of temperature was investigated kinetically by W. Kuhn. He found that in irradiation by the Zn lines (2139–2025) the velocity of reaction increases rapidly with temperature. In fact, with the other conditions remaining the same, the following results are obtained for the velocity of dissociation:

20°	100°	200°	300°	400°	500°
1	1·5	2·2	3·5	6	9

I have recently investigated the absorption spectrum for various temperatures, and find that at 300° C. the bands are very much blurred. At this temperature even the Cd lines (2300–2195) give rise to marked decomposition of ammonia.

When the temperature is raised it is again found that the photochemically effective rays are displaced towards the visible region, parallel with the displacement of the limit of predissociation.

5. *Carbon Disulphide.*—The absorption spectrum of carbon disulphide vapour was first investigated by me in collaboration with Teves.† The analysis of the spectrum was only carried out later along with Kofler.‡ This spectrum consists of two separate regions:

(1) There are several hundred bands between 3980 and 2767 Å. The wave-lengths of the bands between 3786 and 2907 have been published by E. D. Wilson.§ Watson and Parker || have given a classification of the bands with which we are not entirely in agreement.

Until about 2820 these bands are very sharp. After that they gradually become diffuse.

(2) The second region begins at 2385, and stretches far into the ultra-violet. We have measured 49 bands, ending at 2170. At about 2000 Å. the bands of this second region also begin to be blurred.

* *Comptes Rendus*, **178**, 202 (1924).

† Dissertation (Zurich, 1926).

‡ Results not yet published.

§ *Astrophys. Journ.*, **69**, 34 (1929).

|| *Phys. Rev.*, **37**, 1013 (1931).

At ordinary temperatures the irradiation of CS_2 vapour with rays of wave-length exceeding 2900 gives rise to no decomposition. With irradiation at 300° C., on the other hand, the absorption spectrum of sulphur vapour (S_2) is clearly exhibited and a new absorption spectrum occurs far in the ultra-violet.

Even at 367° C. heating without irradiation begins to cause dissociation, and this increases very rapidly as the temperature rises. We obtain the sulphur spectrum and a series of bands which probably correspond to CS. These new bands have a distribution similar to that of the absorption bands of carbon monoxide * at 2060·8, 2060·0, and 2058·6.

The bands which we ascribe to carbon monosulphide have the following wave-lengths:

2386·5, **2385·1**, **2382·5**, **2381·7**, **2379·2**, 2377·5, 2376·1, 2375·1,
2374·4, **2373·7**, **2372·3**, **2371·4**, **2368·6**, 2367·2, **2365·2**, **2364·1**,

with a broad band from 2361 to 2359.

The photochemical reaction, like the thermal reaction, can therefore be written

$$CS_2 \rightarrow CS + S.$$

The predissociation limit $\lambda = 2800$ would give an energy of 102,000 gm. cal. for this reaction. By analogy with SO_2, which dissociates into SO and O at the first predissociation limit, and NO_2, which dissociates into NO and O, we may assume that the resulting sulphur atom will be in the normal $^3P_2$ state.

This assumption is supported by the fact that in the second absorption region we also find a limit at which the bands become diffuse, namely at about 2000 Å. This second limit of predissociation would correspond to a dissociation of CS_2 into CS and S*, the sulphur being in the $^1D_2$ state. Then $S(^3P_2) - S(^1D_2) = 41,000$ cal., which corresponds to 13,300 cm.$^{-1}$; this is quite plausible, seeing that for oxygen $O(^3P_2) - O(^1D_2) = 15,869$ cm.$^{-1}$ (Hopfield) and the corresponding difference must be somewhat less for sulphur.

As regards the first predissociation limit, we have the following further remark to make. W. Jevons † analysed the emission spectrum of CS and obtained the vibration spectrum $1276{\cdot}5\ v' - 6{\cdot}00\ v''^2$

* See V. Henri and Schou, *Zeitschr. f. Physik*, **49**, 814 (1928).

† *Proc. Roy. Soc.*, A, **117**, 351 (1928).

for the lower state v''. From the convergence of this vibration spectrum it is found that for the dissociation of CS we have

$$CS \rightarrow C + S(x) - 193 \text{ Cal.}$$

Now from thermochemical data

$$CS_2 \rightarrow C_{diam} + S_{2\,gas} - 12{\cdot}5 \text{ Cal.}$$
$$C_{diam} \rightarrow C_{gas} - 141 \text{ Cal.}$$

Optically we find that

$$S_2 \rightarrow S + S - 102 \text{ Cal.}$$

We thus conclude that for the dissociation of CS_2 into normal atoms we have

$$CS_2 \rightarrow C + S + S - (12{\cdot}5 + 141 + 102) \text{ Cal.}$$

or

$$C + S + S - 255{\cdot}5 \text{ Cal.}$$

From the first predissociation limit of CS_2 we have

$$CS_2 \rightarrow CS + S - 102 \text{ Cal.}$$

Using Jevons' result, we obtain

$$CS_2 \rightarrow C + S(x) + S - (102 + 193) \text{ Cal.}$$

or

$$C + S(x) + S - 295 \text{ Cal.}$$

That is, the vibrational dissociation of the v'' state of CS must give rise to an excited sulphur atom, the energy of excitation being given by

$$S(x) - S(^3P_2) = 295 - 255{\cdot}5 = 39{\cdot}5 \text{ Cal.};$$

this corresponds to the ^1D-state of sulphur.

The normal dissociation of CS would then take place according to the equation

$$CS \rightarrow C + S(^3P_2) - 153{\cdot}5 \text{ Cal.}$$

This value is in better agreement with the new value for CO (225 Cal.) than the value 195 Cal., which is too high.

Summarizing, we therefore have the following:

$$CO \rightarrow C_g + O(^3P_2) - 225 \text{ Cal.}$$
$$CO \rightarrow C_g + O(^1D) - 270 \text{ ,,}$$
$$CS \rightarrow C_g + S(^3P_2) - 153{\cdot}5 \text{ ,,}$$
$$CS \rightarrow C_g + S(^1D) - 193 \text{ ,,}$$

$$\begin{array}{llll} C_d + \frac{1}{2}O_2 & \rightarrow & CO & + 26{\cdot}3 \text{ Cal.} \\ C_d + O_2 & \rightarrow & CO_2 & + 94{\cdot}5 \quad ,, \\ C_d + \frac{1}{2}S_2 & \rightarrow & CS & - 38{\cdot}5 \quad ,, \\ C_d + S_2 & \rightarrow & CS_2 & + 12{\cdot}5 \quad ,, \end{array}$$

6. *Nitrogen Peroxide* (NO_2).—I have investigated the absorption spectrum of nitrogen peroxide in collaboration with L. Harris; it has also been partially investigated by Mecke and by Lambrey.* Two regions are found.

(1) There is a very complicated spectrum between about 6500 Å. and 2550 Å. From the red end to about 4100 Å. the bands are very sharp and exhibit a very beautiful rotation structure. Between 4100 Å. and 3800 Å. we have a region of transition where the rotation lines become broader and blurred. For $\lambda < 3800$ the bands become distinctly blurred and diffuse and the individual rotation lines can no longer be measured; thus, for example, we have strong continuous bands between 3762 and 3768, 3717 and 3727, again between 3649 and 3658, and so on, the bands becoming more and more blurred and being entirely devoid of fine structure. These diffuse bands can be followed as far as 2700 Å. The maximum absorption lies at about 3450 Å.

(2) The second region extends from 2580 Å. far into the ultra-violet (the last band measured being at 2083 Å.). It consists first of four bands with a very sharp fine structure; each of these bands has a sharp band-head and consists of 40–90 fine lines extending towards the visible region. For these four bands the positions of the band-heads and the final lines are as follows:

D	Band-head	2576·2	Last line	2586·4
C	,,	2538·5	,,	2545·4
B	,,	2491·4	,,	2524·2
A	,,	2459·3	,,	2486·4

In fig. 5 (Plate IV) we give the photograph of a part of the absorption spectrum and in fig. 6 the microphotograph of a part of the bands B, A, and I.

The bands B, C, and D consist of a double series of very sharp lines which definitely fall into two series, a stronger one (indicated by the numbers 1, 2, 3, 4, 5, 6 on the microphotograph) and a feebler one lying in between. The stronger series corresponds to rotation about the axis of symmetry of the triangular NO_2 molecule

* *Comptes Rendus*, **188**, 251 (1929).

and the feebler to rotation about an axis at right angles to this.
The distribution of the lines of the intense series is very

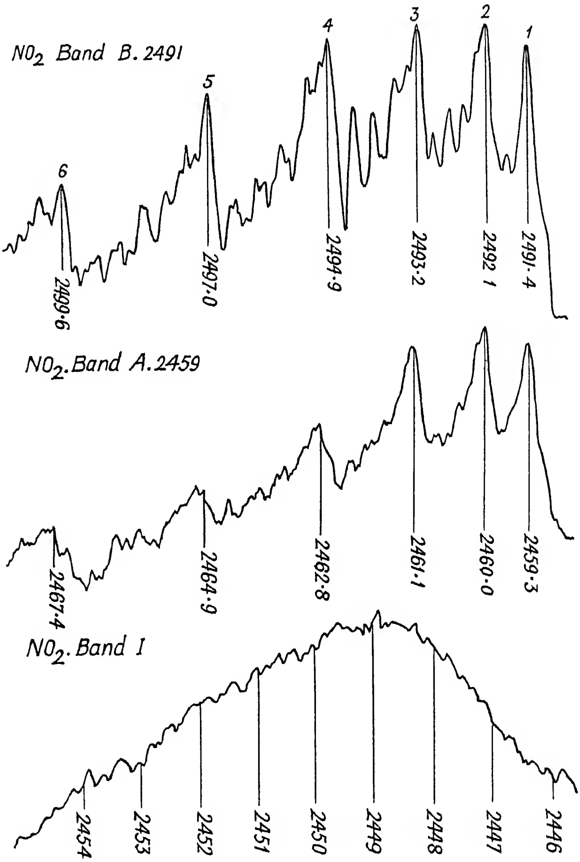


Fig. 6

accurately that of a Q-branch. Thus e.g. for the band B the distribution is represented by

$$Q(m) \ldots \nu = 40{,}129{\cdot}7 - 3{\cdot}7\ \mathrm{m.}^2,$$

where $m = 1, 2, \ldots, 12$. The terms from $m = 3$ onward are doubled and the separation increases with m. That is, there are two branches Q and Q′.

The lines of the series lying in between are much feebler and their distribution is complicated. We see clearly, however, that

these lines are piled up against every term of the more intense series; here, then, we have the same type of doubled rotation structure as in the case of formaldehyde.

The same double rotation structure appears in the band A but the lines are no longer so sharp; this is seen very clearly on comparing the two microphotographs B and A.

Further on in the ultra-violet we obtain 15 more bands (I to XV), which are all quite blurred and continuous. As will be seen from the photograph (fig. 5), the transition here is very abrupt. Band I exhibits four or five feeble fluctuations which are easily seen in the microphotograph; the following bands II to XV, however, do not exhibit these fluctuations. These bands have a breadth of from 10 to 20 Å. and are distributed at regular intervals. They are vibrational bands without rotational quantization.

We see therefore that in the case of NO_2 there are two limits of predissociation, the first being indefinite and occurring between 4100 and 3800, and the second very sharp at 2459.

The photochemical dissociation of NO_2, which takes place quantitatively according to the equation

$$NO_2 \rightarrow NO + O,$$

has been investigated by Norrish * and the quantum yield γ determined for various wave-lengths. He finds

for radiation	between	5750 and 4360	no	reaction	($\gamma = 0{\cdot}0$)
,,	,, of	4050	feeble	,,	($\gamma = 0{\cdot}74$)
,,	,, of	3650	strong	,,	($\gamma = 2{\cdot}10$)
,,	,, between	3160 and 2700	strong	,,	($\gamma = 2{\cdot}07$).

The reaction accordingly sets in at the very region of transition where the bands begin to be somewhat blurred (between 4100 and 3800), while it is just where the bands are quite diffuse (3650) that the reaction is very strong.

Fluorescence investigations have shown that blue rays (4360) and violet rays (4050) produce strong fluorescence, whereas ultra-violet rays (3650) give rise to no fluorescence.

The predissociation between 4100 and 3800 gives the energy of the reaction

$$NO_2 \rightarrow NO + O(^3P_2).$$

As the limit is not sharp, the energy cannot be stated exactly; it

* *Journ. Chem. Soc.*, 1158, 1604, 1611 (1929).

lies between 69·8 and 75·3 Cal. The predissociation limit in the second region is very sharp and occurs at the wave-length 2459 Å. This limit corresponds to a dissociation in which an excited oxygen atom in the $^1D_2$ state is produced.

We accordingly have

$$NO_2 \rightarrow NO + O(^1D_2) - 116{\cdot}2 \text{ Cal. } (2459 \text{ Å.}).$$

Now according to Frerichs,* Hopfield,† and Paschen‡ the terms of oxygen are as follows: $^3P_2 = 109{,}837$, $^1P_1 = 109{,}679$, $^3P_0 = 109{,}610$, $^1D_2 = 93{,}962$, and $^1S_0 = 76{,}044$ cm.$^{-1}$; that is,

$$O(^3P_2) - O(^1D_2) = 15{,}868 \text{ cm.}^{-1} = 45{\cdot}4 \text{ Cal.}$$

From this it is calculated that the energy required for the normal dissociation into NO and $O(^3P_2)$ is $116{\cdot}2 - 45{\cdot}4 = 70{\cdot}8$ Cal.; this corresponds to the wave-length 4040 Å., i.e. falls in the transition region of the first predissociation.

From the thermochemical equation

$$NO_2 \rightarrow NO + \tfrac{1}{2}O_2 - 13{\cdot}5 \text{ Cal.}$$

it is calculated that the energy required for the dissociation of the oxygen molecule into two normal oxygen atoms amounts to $2(70{\cdot}8 - 13{\cdot}5) = 114{\cdot}6$ Cal.

7. *Sulphur Dioxide* (SO_2) possesses an absorption spectrum consisting of three regions. I investigated it first with Teves in 1925 and subsequently with K. Wieland.§

The first region is exhibited with high pressures (1 atm. or over, with $d = 100$ cm.) and consists of a number of very fine bands with sharp rotation lines; it extends from 3950 to 3400 Å.

The second region extends from 3480 to about 2400, appears even at a pressure of 0·1 mm. (for $d = 100$ cm.), has a maximum at 2850, and reaches its extreme limit at a pressure of 700 mm. The bands in this region have often been measured already. In a recent paper W. Watson and E. Parker ‖ have interpreted this spectrum, assigning two frequencies 1381 and 1157 cm.$^{-1}$ to the normal molecule and 381·1 and 436·7 cm.$^{-1}$ to the excited molecule. As we have made clear elsewhere, we do not wholly agree with this classification.

* *Phys. Rev.*, **34**, 1239 (1929); **36**, 398 (1930).

† *Phys. Rev.*, **37**, 160 (1931).

‡ *Naturwiss.*, **18**, 752 (1930); *Zeitschr. f. Physik*, **65**, 1 (1931).

§ Results in course of publication.

‖ *Phys. Rev.*, **37**, 1013 (1931).

The bands of this region above 2800 are very sharp and exhibit a good rotation spectrum, especially if the absorption spectrum is photographed at $-80°$ C.

Between 2800 and 2680 we have a region of transition, where the rotation lines become blurred and the bands broaden out. Towards the ultra-violet the bands become more and more blurred, so that in the region of 2550 and beyond nothing appears but thoroughly diffuse continuous bands.

Here, therefore, it is impossible to give a definite limit of predissociation. The transition region corresponds to an energy of 102 to 107 Cal., the entirely blurred bands (2550) to an energy of 111 Cal.

The third region appears at low pressures of 0·02 to 10 mm. It extends from 2445 far into the ultra-violet; we were able to trace it as far as 1935, but it goes still farther. Above 2100 we were able to measure more than 120 band-heads accurately on photographs with large dispersion (by E_1 Hilger spectrograph); the bands from 2445 to 2100 exhibit a very beautiful sharp rotation structure. These bands may be satisfactorily represented by three fundamental frequencies (1360, 1156, and 518 cm.$^{-1}$) of the normal molecule and the frequencies 960 and 379·5 cm.$^{-1}$ of the excited molecule. (The Raman frequencies are 1340, 1146, and 524 and the infra-red frequencies 1360, 1152, and 606 cm.$^{-1}$). With the smaller (Zeiss) spectrograph we photographed still further bands; sharp bands with quantized rotation are obtained down to 1950, after which the bands very rapidly become diffuse.

As with NO_2 and CS_2, therefore, the second limit of predissociation is very sharp; it corresponds to an energy of 147 Cal.

The occurrence of predissociation may be explained by the following reactions:

$$SO_2 \rightarrow SO + O\,(^3P_2)$$
$$SO_2 \rightarrow SO + O^*\,(^1D_2).$$

As the second predissociation limit is sharp we may with fair accuracy take the energy of the second reaction as 147 Cal.

Then as

$$O^*\,(^1D_2) - O\,(^3P_2) = 45{\cdot}4 \text{ Cal.}$$

we conclude that for the normal dissociation of SO_2 we have

$$SO_2 \rightarrow SO + O\,(^3P_2) - 101{\cdot}6 \text{ Cal.};$$

this corresponds to $\lambda = 2826$ Å. Now we have seen that the tran-

sition region of the first predissociation begins at about 2800 Å., i.e. very near the above value.

We may use this value to calculate the energy of dissociation of oxygen.* Thermochemically, in fact, we have (Ferguson)

$$\tfrac{1}{2}S_2 + O_2 \rightarrow SO_2 + 83 \text{ Cal.}$$

Optically from predissociation we have

$$S_2 \rightarrow S + S - 102{\cdot}4 \text{ Cal.}$$

In a previous paper written in collaboration with F. Wolff † I have calculated from the convergence limit that

$$SO \rightarrow S + O - 148 \text{ Cal.}$$

The energy of dissociation of oxygen is then equal to

$$148 + 101{\cdot}6 - \frac{102{\cdot}4}{2} - 83 \quad \text{or} \quad 115{\cdot}4 \text{ Cal.}$$

This value represents the upper limit; it lies very near that calculated from NO_2(114·6).

The absorption spectrum of SO_2 is strongly affected by rise of temperature. This temperature effect consists in the bands of the second region (which we have alone investigated) becoming much more blurred at the ultra-violet end and the predissociation limit being displaced towards the visible end. Thus e.g. at 340° C. there is merely one broad continuous band between 2734 and 2740, whereas at 18° five bands can easily be measured. At 340° C. no rotation lines can be measured below 2900, owing to their being blurred; it is only at 2920 that the rotation lines appear clearly, and these lines become clearer and clearer as we approach the visible region, just as sharp as in the spectrum at 18°.

At 530° no discrete bands at all are seen below 2800 Å., but merely a continuous region of absorption; then follow feeble fluctuations, which recur periodically. It is only at 2900 that these fluctuations become clearer, and the bands can then be seen clearly, but no rotation structure is exhibited till 3085 Å. is reached.

In fig. 7 we give a part of the microphotograph between 3085 and 2833 for the temperatures 18° and 530° C. The SO_2 vapour was

* V. Henri, *Nature*, **125**, 275 (1930).
† *Journ. Phys. et Rad.*, **10**, 81 (1931).

enclosed in a quartz tube 30 cm. long at a pressure of 3 mm. at 18° and the tube was brought to various temperatures. There is therefore no question of the widening of the lines being due to pressure.

8. *Sulphur*.—I first investigated the absorption spectrum of sulphur vapour at various temperatures between 200° and 1100° C. in collaboration with Teves (1924) and subsequently with D'Or, de Hemptinne, and Almasy. This spectrum contains several regions and its analysis cannot yet be regarded as complete. Papers have recently been written on the spectrum of the sulphur molecule by Rosen,* Schwings,† H. H. Van Iddekinge,‡ Curtis and Tolansky,§ and S. M. Naudé and A. Christy,|| and yet our knowledge of many of the details is very unsatisfactory. A detailed discussion and

Fig. 7.—SO_2 at 18° C. and 530° C.

analysis of this spectrum will be given in a longer paper elsewhere. Here I shall only report on the chief features of the predissociation.

In the molecular spectrum of sulphur vapour four regions may be distinguished.

The first of these is situated between the visible and the long-waved ultra-violet (investigated between 8000 Å. and 4833 by Curtis and Tolansky, between 4575 and 3175 by Rosen, and between 4500 and 3400 by us). In absorption this spectrum consists of more than a hundred bands which may readily be classified in series; it is a finely developed vibration spectrum, but the bands are blurred and exhibit no rotation structure.

Graham formerly ascribed this spectrum to a complicated molecule S_6 or S_4, because it vanishes with rise of temperature. Rosen ascribed it to the S_2 molecule, because the vibration frequencies seem to be the same as in the second ultra-violet region, but the accuracy of Rosen's measurements is not very great

* *Zeitschr. f. Physik*, **43**, 69 (1927); **48**, 545 (1928); **52**, 16 (1928).

† *Zeitschr. f. Physik*, **61**, 681 (1930); *Comptes Rendus*, **189**, 982 (1928); ibid. **190**, 965 (1930); *Bull. Acad. Polonaise*, p. 616 (1929).

‡ *Nature*, **125**, 858 (1930).

§ *Phil. Soc., Durham Univ.* (1931).

|| *Phys. Rev.*, **37**, 490, 903 (1931).

($\pm$ 20 cm.$^{-1}$) and besides not nearly all the bands in this region have been classified.

We have made exposures at the same temperatures and pressures in tubes 2, 5, 5, 10, and 40 cm. long, the pressures being measured by a Bodenstein quartz-spiral manometer. The smaller the pressure, i.e. the greater the length of the vapour column, the lower the temperature at which the spectrum vanishes.

Thus e.g. with a concentration of 40 mg. sulphur in 1000 c.c. at 400° C. we obtain these bands with a column of vapour only 2·5 cm. long. The bands extend from 4500 to 3600 Å.; from thence a region of continuous absorption extends far into the ultra-violet and no bands with rotation structure are obtained. If we now raise the temperature somewhat (to 460°) the bands with fine structure appear in the medium and remote ultra-violet.

If we use a quarter the concentration (10 mg. per litre) and a column of vapour four times as long (10 cm.) and again make exposures at 400° C., we no longer obtain the blurred bands between 4500 and 3600, but beautiful bands with a very sharp rotation structure appear in the medium ultra-violet between 3400 and 2900.

What we have is a definite reversible equilibrium between S_2 molecules and (probably) S_4 molecules. In my opinion the first absorption region corresponds to these S_4 molecules.

The S_6 and S_8 molecules give a continuous spectrum in the far ultra-violet.

The second absorption region extends from 4100 to the remote ultra-violet (measured by us down to 2300). It consists of a very large number of fine bands which may be classified as a vibration spectrum.

Between 4100 and 2793·2 Å. we have a very complicated rotation spectrum which has recently been analysed by Naudé and Christy and consists of 3P- and 3R-branches, i.e. corresponds to the transition $^3\Sigma - {}^3\Sigma$ of the molecule S_2.

The region from 4100 to about 3100 has a different vibration structure; it probably corresponds to transitions from Σ-states to Π-states, for in this region we obtain definite Q-branches of rotation.

At 2793·2 Å. (equivalent to 35,790·7 cm.$^{-1}$ or 102·4 Cal.) the spectrum suddenly changes. Up to this limit, in fact, the bands are very sharp, with rotation structure, as we see e.g. in fig. 8 (Plate IV), which corresponds to the region from 3100 to 3021 Å. The last sharp line is 2793·2; then the bands suddenly become blurred. Each vibration group, denoted in fig. 8 (Plate IV) and fig. 9

(Plate V) by the figures 0, 1, 2; 14, 15, 16, consists of 20 to 25 narrow bands without any fine structure. These are seen clearly in fig. 9 (0·1 mg., $v = 11{\cdot}3$ c.c., $d = 4{\cdot}5$ cm., T = 670° C.).

These narrow bands are distributed very regularly according to a parabolic formula, as given in the following table.

TABLE II

Number of Band	Formula	
10	$36{,}104{\cdot}0 - 0{\cdot}4\,n^2$	n from 13 to 28
11	$36{,}469{\cdot}6 - 0{\cdot}4\,n^2$	,, ,, 13 ,, 29
12	$36{,}829{\cdot}0 - 0{\cdot}4\,n^2$	,, ,, 14 ,, 37
13	$37{,}201{\cdot}0 - 0{\cdot}4\,n^2$	,, ,, 10 ,, 38
14	$37{,}549{\cdot}0 - 0{\cdot}4\,n^2$	,, ,, 12 ,, 37
15	$37{,}907{\cdot}0 - 0{\cdot}4\,n^2$	,, ,, 6 ,, 35
16	$38{,}242{\cdot}0 - 0{\cdot}4\,n^2$	,, ,, 6 ,, 28

In fig. 10 we give a number of microphotographs of the bands 9 to 17. In the lower microphotographs from 2818 to 2793 we see

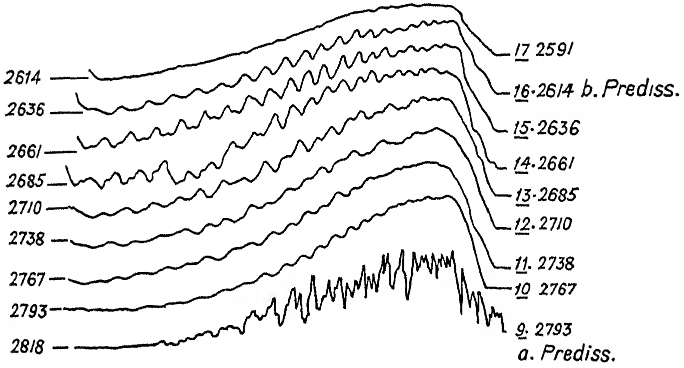


Fig. 10.—S_2 Bands

a well-developed fine structure; the remaining bands exhibit the narrow bands without fine structure. At the band 16 (2614 Å.) there is a second sudden change in the character of the spectrum; here the narrow bands also vanish and we obtain a uniform continuous band reaching to 2591 (band 17); then follow other bands at intervals of about 360–320 cm.$^{-1}$ down to about 2300 Å.

In the remote ultra-violet a new absorption region begins at about 2580 Å.; it is superposed on the region just discussed and its structure has not yet been cleared up. This region consists of narrow bands, mostly only 2–3 cm.$^{-1}$ across, which extend to beyond 2300 Å.

These bands are sharper the higher the temperature, above 800° C., that is to say: they are particularly well exhibited at 1000° and 1100°.

All these regions of the absorption spectrum overlap to some extent, which makes their analysis fairly difficult.

We see, then, that there are two definite limits of predissociation: *a* at 2793·2 Å., *b* at 2614 Å.

It is very plausible to interpret the first physically as corresponding to the normal dissociation of the S_2 molecule. That is,

$$S_2(^3\Sigma) \rightarrow S(^3P_2) + S(^3P_2),$$

for which 102·4 Cal. are required. This value is in agreement with the value 103·6 Cal. obtained thermally by Budde.* Budde's method, however, does not permit of the energy of dissociation being measured with great accuracy.

As regards the second limit *b*, it must correspond either to dissociation of a sulphur molecule into another state or, better, to the intersection of a potential curve of the $S_2(^3\Sigma)$ molecule with the repulsion curve of the potential of two sulphur atoms which approach one another but do not form a molecule.

One point remains to be mentioned: the photochemical reaction between sulphur vapour and H_2.

It was found by Taylor, and subsequently by Teves and myself, that rays of wave-length exceeding 2800 do not give rise to formation of H_2S; on the other hand, H_2S is at once obtained by irradiation with rays from the first region of predissociation, that is, the sulphur molecules are rendered chemically active by the rays of the predissociation region.

9. *Benzene.*—As a final example I shall discuss the benzene spectrum and in particular its variation with temperature.

The absorption spectrum, as is well known, consists of a number of sharp bands extending from 2667 to 2000 at regular intervals of 921·7 cm.$^{-1}$. Each of these bands A, B, C, D, E, F, &c., consists of subsidiary bands at intervals of 162 cm.$^{-1}$ (B′, B″, B‴; C′, C″, C‴, &c.).

If a small quantity of benzene vapour is enclosed in a quartz tube ($p = 5$ mm. at 19° C., $d = 30$ cm.) and the spectrum is then photographed at various temperatures, it is found that the spectrum varies very markedly with temperature. The effects of a rise in temperature begin at the ultra-violet end and spread farther towards the visible region the higher the temperature; as the temperature

* *Zeitschr. f. anorg. Chemie*, 78, 169 (1912).

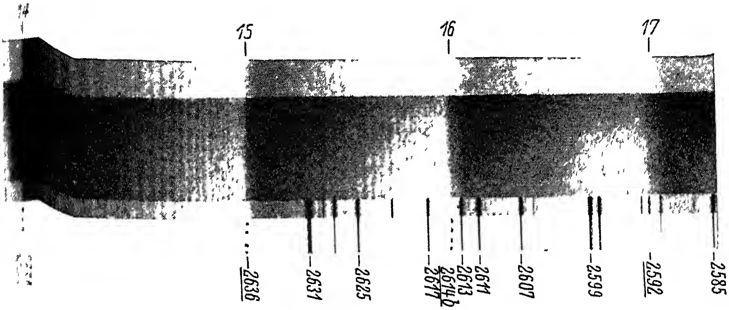
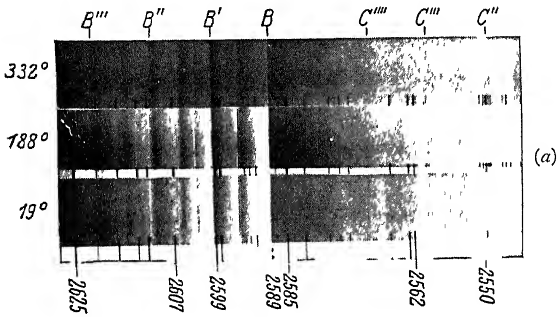


Fig. 9.—S_2, predissociated



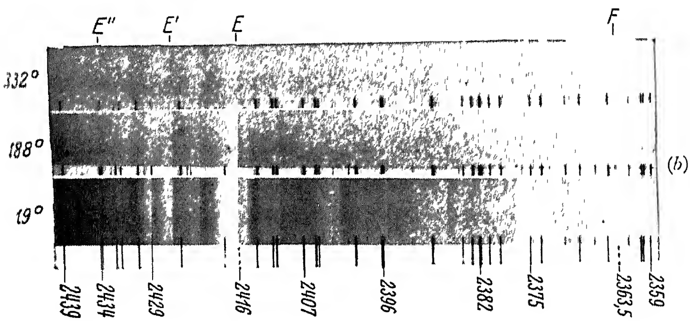


Fig. 11 *a*, *b*—Benzene Vapour

$p = 5$ mm, $d = 30$ cm, $t = 19°$, $188°$, and $332°$ C

rises the bands become more and more blurred. This is clearly shown in fig. 11 (Table V) where we give two spectra, one at 19° and one at 332° C. In the spectra *b* between 2439 and 2359 the bands of group F are quite blurred at 332° C. and begin to be blurred even at 188°. Groups E and D (spectra *b*) are particularly blurred at 332°. The group C and B, however, are quite sharp at 332°, but if the temperature is raised to 440° they also become quite blurred.

Broadly speaking, we may say that a rise of temperature of 144° produces a displacement of the limit of predissociation in benzene through about 1000 to 2000 cm.$^{-1}$, a displacement which corresponds to an energy of 2850 to 3400 calories. As a result of this rise in temperature the kinetic energy of the molecule is increased by $c_v(T_1 - T_2) = c_v \cdot 144$; if we relate this to the displacement of the limit of predissociation, it would follow that the specific heat of benzene vapour is $c_v = 20$ to 24. The specific heat of benzene vapour is 21·8 at 20° and 25·8 at 100°; thus the displacement of the limit of predissociation could be inferred from the magnitude of the specific heat.

A perfectly general result, which we have observed in many substances, is that the greater the molecular heat C_v, the more marked is the temperature effect.

Summary.

1. The occurrence of predissociation in absorption spectra is a perfectly general phenomenon with both simple and polyatomic molecules.

2. In many cases more than one region of predissociation occurs. Predissociation may set in gradually or suddenly.

3. The limit of predissociation gives the upper limit for the energy of dissociation of a molecule. If predissociation sets in gradually the energy of dissociation must be reckoned as from the beginning of the region of predissociation, i.e. the position where the rotation lines begin to broaden out (NO_2, CS_2, SO_2, HCOH).

4. The number of the regions of predissociation corresponds to the varying possibilities of dissociation of the molecule. In triatomic molecules AB_2 the energies involved in the processes

$$AB_2 \rightarrow AB + B$$

and

$$AB_2 \rightarrow AB + B^*$$

are in general obtained from the limits of predissociation. The

limit for the dissociation in which an excited atom B* is formed is much sharper than the first limit of predissociation.

5. A rise of temperature displaces the limits of dissociation towards the visible region. The greater the molecular heat of the substance, the greater is this temperature displacement.

6. The rays of the region of predissociation give rise to photochemical reaction or chemical sensitization of the molecules in all the cases which have been investigated.

7. The physical explanation of the phenomena of predissociation must consist in a very marked shortening of the length of life of the excited molecules. This length of life must be of the order of magnitude of the period of rotation of the molecules. This shortening of the life of the molecule is explained by the possibility of the excited molecules reaching the stable final state by various ways.

On Predissociation

R. DE L. KRONIG, GRONINGEN

As is well known, the motion of diatomic molecules may be thought of as arising from the superposition of electronic motion, nuclear vibration, and nuclear rotation. The mathematical basis for the possibility of this analysis of the motion is the fact that to a considerable degree of accuracy a kind of separation of the wave equation of the system may be brought about by the introduction of suitable co-ordinates.* For this purpose it is best to choose two systems of rectangular co-ordinates with their origin at the centre of gravity of the nuclei, one set of co-ordinates (x, y, z) being fixed in space, and the other (ξ, η, ζ) being such that the ζ-axis lies along the line joining the two nuclei, and the ξ-axis lies in the xy-plane. If we then describe the positions of the electrons by means of their rectangular co-ordinates ξ_k, η_k, ζ_k (and possibly their spin co-ordinate σ_k with respect to the ζ-axis), and the positions of the nuclei by means of the internuclear distance ρ and the two polar angles θ and ψ which fix the direction of the ζ-axis in the system of co-ordinates x, y, z, the wave equation may be satisfied by a function of the form

$$\Psi = \Phi(\xi_k, \eta_k, \zeta_k, \sigma_k, \rho)\mathrm{P}(\rho)\Theta(\theta, \psi),$$

provided certain terms which are in general very small are neglected.

Here Φ is the normalized wave function of the electronic motion, the nuclei being regarded as fixed centres of force at a distance ρ apart. Like the associated energy $V(\rho)$, Φ contains ρ as a parameter. The function Θ is a solution of the wave equation of the symmetrical top, an equation which also depends on J, the rotational quantum

* In this connexion see J. H. van Vleck, *Phys. Rev.*, 33, 467 (1929), and R. de L. Kronig, *Band Spectra and Molecular Structure* (Cambridge University Press, 1930).

number of the molecule. Finally, P must satisfy the equation

$$\frac{d^2P}{d\rho^2}+\frac{2}{\rho}\frac{dP}{d\rho}+\frac{8\pi^2\mu}{h^2}[W-V_J(\rho)]P=0,$$

which also determines the energy W. Here

$$\mu=\mu_1\mu_2/(\mu_1+\mu_2)$$

is the reduced nuclear mass, and

$$V_J(\rho)=V_0(\rho)+\frac{h^2}{8\pi^2\mu\rho^2}J(J+1),$$

where $V_0(\rho)$ is identical with $V(\rho)$, the above-mentioned energy function of the non-rotating molecule, except for a correction which is in general negligible and in any case is independent of J.

In a given stable electronic state $V_0(\rho)$ as a function of the internuclear distance ρ is represented, as is well known, by a curve of

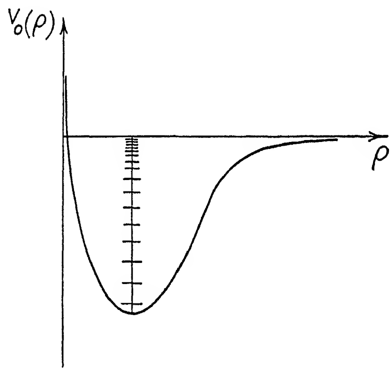


FIG. 1

the type shown in fig. 1. If the nuclei are permitted to vibrate along the line joining them about the equilibrium position corresponding to the minimum of the curve, a series of vibrational levels, distinguished by a vibrational quantum number v, are superposed on the electronic state; in the figure these are indicated by horizontal strokes on the ordinate of the minimum of the energy curve. Owing to the zero-point energy required by the wave mechanics, the lowest of these levels, $v=0$, lies somewhat above the minimum of the energy curve. The vibrational levels converge towards the horizontal asymptote of the energy curve as a limit. The position of convergence corresponds to the dissociation of the molecule

into two subsidiary systems (atoms or ions in definite stationary states) as a result of increased energy of vibration. Above the limit there is a continuous region of energy values which mean a dissociation of the molecule into two subsidiary systems with a value of the kinetic energy different from zero.

If we also let the nuclei be free to rotate, the term $h^2J(J + 1)/8\pi^2\mu\rho^2$, which is positive and proportional to $1/\rho^2$ and is due to

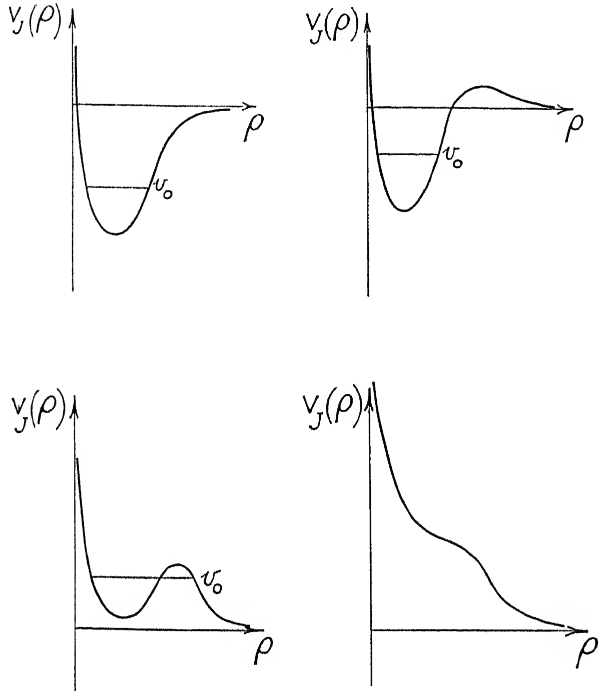


Fig. 2

the centrifugal forces, enters into the energy curve determining the nuclear vibration, in addition to the function $V_0(\rho)$ shown in fig. 1; this new term is greater, the faster the molecule rotates.

If the energy curve $V_0(\rho)$ for the non-rotating molecule approaches the asymptote more rapidly than $1/\rho^2$ when ρ is large, the above-mentioned additional term, as has been emphasized by Oldenberg * in particular, gives rise to a resultant energy curve $V_J(\rho)$; so long as J is not too large, this curve has a maximum as well as a minimum, but for very large values of J it has only a point of inflexion. This

* Oldenberg, *Zeitschr. f. Physik*, 56, 563 (1929).

we see from fig. 2, where the curves are drawn for various values of J.

Like the non-rotating molecule, the rotating molecule has a system of vibrational levels, and in fact a different system for every value J, corresponding to the energy curves $V_J(\rho)$ modified by the centrifugal forces. If we now fix our attention on a definite vibrational level, say that distinguished by the vibrational quantum number v_0, and let J increase, we see that the energies corresponding to the successive values of J will also increase, as indicated by the horizontal lines in fig. 2. If J is chosen sufficiently large the level v_0 finally comes to lie above the asymptote, as in fig. 2. According to the wave mechanics, however, there is then a definite probability that the nuclei will pass through the energy maximum and fly apart as a result of the centrifugal forces; for energy values *above* the asymptote the length of life of the molecule is finite, and the energy values become blurred.

This phenomenon is the decomposition of molecules by rotation first investigated by Oldenberg.* As this has already been discussed in detail for mercury hydride in Miss Sponer's paper (p. 118), it is only briefly mentioned here in order to show that it is brought out by the mathematical discussion even at the stage of approximation for which the wave equation is still separable.

It is otherwise with the real predissociation discovered by Henri and Teves.† In many cases it happens that the energy curves $V_0(\rho)$ of two electronic states A and B of a diatomic molecule run as shown in fig. 3, i.e. that they converge towards different asymptotes PP and QQ. The discrete levels of B above PP are then situated in a region of energy in which the proper values of A are already continuous. The molecule in these levels of B thereby acquires the possibility, so far as energy is concerned, of spontaneous transition to the continuous levels of A of the same energy, i.e. of dissociation into atoms without radiating, as was emphasized by Bonhoeffer and Farkas ‡ and also by the writer.§ The possibility of such transitions actually taking place depends on the presence of the terms which have hitherto been neglected in the wave equation of the molecule; for this phenomenon, then, it is essential to take these terms into account, and this may be conveniently done by

* Oldenberg, *Zeitschr. f. Physik*, **56**, 563 (1929).

† Henri and Teves, *Nature*, **114**, 894 (1924); *Comptes Rendus*, **179**, 1156 (1924).

‡ Bonhoeffer and Farkas, *Zeitschr. f. phys. Chemie*, **134**, 337 (1927).

§ Kronig, *Zeitschr. f. Physik*, **50**, 347 (1928).

methods for the calculation of perturbations. These terms are thereby decomposed into terms arising from a sort of coupling of electronic motion and nuclear vibration even when nuclear rotation is suppressed, and additional terms resulting entirely from the interaction between electronic motion and nuclear rotation.

In order that non-radiating transitions of the kind under consideration may arise from a discrete energy level to any appreciable extent, it is not sufficient that a level of the same energy associated

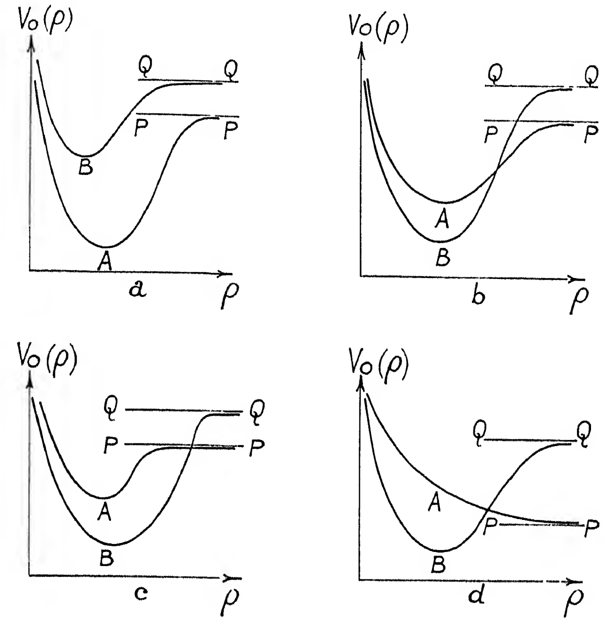


Fig. 3

with a continuous energy region should exist; on the contrary, as has likewise been shown by the author,* further conditions must be fulfilled:

1. The two levels of the same energy must also have the same value for the total angular momentum; in other words, in spontaneous decomposition the total angular momentum of the molecule does not change—which might be expected a priori.

2. They must belong to electronic states in which the angular momenta of the electrons about the line joining the nuclei do not differ by more than one unit.

* Kronig, *Zeitschr. f. Physik*, **50**, 347 (1928).

3. They must have the same symmetry with respect to reflection in the origin.

4. They must have the same symmetry with respect to interchange of the point co-ordinates of the electrons, i.e. they must belong to electronic states of the same multiplicity.

5. In homonuclear molecules (molecules with two nuclei identical) the symmetry with respect to interchange of the point co-ordinates of the nuclei must also be the same.

If we ask whether the limit of convergence of the vibrational levels of an electronic state A has any bearing on the predissociation of an electronic state B with higher discrete levels, we must first know what products arise from the molecular dissociation corresponding to this limit. According to Wigner and Witmer,* we can then theoretically state what other electronic states of the molecule can arise when these products are brought together and are therefore associated with the same limit, and we can also predict their properties as regards angular momentum of the electrons about the line joining the nuclei, symmetry, and multiplicity. If among these electronic states there are none for whose levels the conditions 1–4 (or 1–5 for molecules with identical nuclei) can be simultaneously fulfilled, the limit does not affect the predissociation.

The question further arises how the probability of decomposition is affected by the mutual position of the energy curves in fig. 3, if the conditions 1–4 or 1–5 are fulfilled. Franck and Sponer † and Herzberg ‡ have investigated this problem in greater detail, and have put forward a rule which is analogous to the Franck-Condon principle for transitions involving radiation. According to these workers, the probability of predissociation is only appreciable if the curves of fig. 3 intersect and the point of intersection lies about the same height as the limit of predissociation or above it, and this for the levels in the neighbourhood of the point of intersection. If the two electronic states A and B are stable, i.e. both have minima, the three cases of fig. 3, *a–c* are essentially distinct. It is only in the last of these three cases that the probability of dissociation can become large, and that for levels lying at about the same height as the point of intersection. On the other hand, in the case where the one electronic state is unstable, i.e. corresponds to

* E. Wigner and E. E. Witmer, *Zeitschr. f. Physik*, **51**, 859 (1928).

† Franck and Sponer, *Göttinger Nachr.*, 1928, p. 241.

‡ Herzberg, *Zeitschr. f. Physik*, **61**, 604 (1930).

a repulsion curve as in fig. 3*d*, the point of intersection necessarily lies above PP, and then the probability of decomposition can again become considerable for those levels which have about the same energy as the point of intersection. In general, then, it is only in the case of fig. 3*c* that the predissociation limit will appear sharp in the spectra and be obtainable from the latter.

Finally, we may inquire how the probability of decomposition varies with the rotational quantum number J. According to the author's investigations,* it appears that for transitions in which the angular momentum of the electrons about the line joining the nuclei remains unaltered, the probability of decomposition is practically independent of J, whereas for transitions in which the angular momentum changes by a unit, it increases as the square of J.

The finite length of life of the levels for which the possibility of predissociation exists is manifested in the spectrum in two ways. In the first place, it gives rise to an indefiniteness in the energy values, and indeed under favourable circumstances, as the author * has shown, the indefiniteness is comparable with the distance between successive rotational levels, so that the rotation structure of the corresponding bands appears blurred. If the levels in question appear as initial states of band lines, these are also decreased in intensity, as some of the molecules decompose without radiating before a radiation transition takes place.

We now come to a discussion of the experimental material. In the case of S_2, Henri and his pupils † found in investigating the absorption spectrum that the bands leading to the levels of the excited electronic state which lie above a definite energy value are diffuse. These levels, then, are in a state of predissociation. According to Van Iddekinge ‡ the bands which are diffuse in absorption are almost entirely absent in emission owing to the short length of life of the molecule. The same fact had previously been observed by Bonhoeffer and Farkas § in the spectrum of ammonia. The re-occurrence of the rotational fine structure in the case of the higher discrete levels of the excited state, as observed

* Kronig, *Zeitschr. f. Physik*, **50**, 347 (1928).

† Henri and Teves, *Nature*, **114**, 894 (1924); *Comptes Rendus*, **179**, 1156 (1924); Henri and Wurmser, *Journ. de Phys.*, **8**, 289 (1927); Teves, Dissertation (Zürich, 1926).

‡ Van Iddekinge, *Nature*, **125**, 858 (1930).

§ Bonhoeffer and Farkas, *Zeitschr. f. phys. Chemie*, **134**, 337 (1927).

by Rosen,* is according to Franck and Sponer † and Herzberg ‡ to be understood as meaning that for the levels in question the probability of dissociation again becomes small, because they lie sufficiently far removed from the point of intersection of the potential curves. A detailed discussion of predissociation in the S_2 spectrum has recently been given by Christy and Naudé.§ Similar phenomena have also been observed in the spectrum of P_2 by Herzberg.||

Magnesium hydride yields another particularly interesting example of predissociation. Here Pearse ¶ finds a band (which he calls the β-band) corresponding to a transition $v = 0 \rightarrow v = 0$ from a $^2\Pi$-state to a $^2\Sigma$-state. Now it is found that the P- and R-branches of this band break off suddenly after the 10th line, whereas the Q-branch can be followed to the 25th line. If we take no account of the spin, which here is so loosely coupled that its effect on the motion may be neglected, then every rotational level of the $^2\Pi$-state is doubled (Λ-doubling). The lines of the P- and R-branches start from one of the component levels, those of the Q-branch from the other (see fig. 4).** The levels then fall under the headings of even and odd, and in the figure are distinguished by crosses and circles respectively.

Now according to the author †† the peculiar behaviour of the three branches may be understood if we assume that between the tenth and eleventh rotational levels of the vibrational level $v = 0$ in the $^2\Pi$-state there lies the limit of convergence of a $^2\Sigma$-state, which we shall denote by $^2\Sigma'$ to distinguish it from the final state of the band under consideration. Its rotational levels, like those of $^2\Sigma$, are alternately odd and even for successive values of K, even in the region where the vibrational energy is continuous. With a given K of the $^2\Sigma'$-state, then, only one of the two component levels resulting from Λ-doubling can satisfy conditions (1) and (3), i.e.

* Rosen, *Zeitschr. f. Physik*, **43**, 69 (1927); **48**, 545 (1928).

† Franck and Sponer, *Göttinger Nachr.*, 1928, p. 241.

‡ Herzberg, *Zeitschr. f. Physik*, **61**, 604 (1930).

§ Christy and Naudé, *Phys. Rev.*, **37**, 903 (1931).

|| Herzberg, *Nature*, **124**, 239 (1930).

¶ Pearse, *Proc. Roy. Soc.*, A, **122**, 442 (1929).

** As the spin is assumed to be loosely coupled, the rotational levels are characterized by the total angular momentum of the molecule without spin, which we denote by K; K then takes the place of J in condition (1) above.

†† Kronig, *Zeitschr. f. Physik*, **62**, 300 (1930).

can be such that the rotational level K of the $^2\Sigma$-state which coincides with it possesses the same reflection symmetry.

It is only for this level that the probability of predissociation arises. The differing behaviour of the three branches is thus explained. In order to obtain agreement with experiment, we have to assume that a rotational level K of the $2\Sigma'$-state has the same reflection symmetry as the rotational level K of the $^2\Sigma$-state, for then the initial states of the P- and R-branches are those for which predissociation becomes possible.

If we suppose that the $^2\Sigma$-state arises from a normal Mg atom in the ^1S-state and a normal H atom in the ^2S-state, it is probable

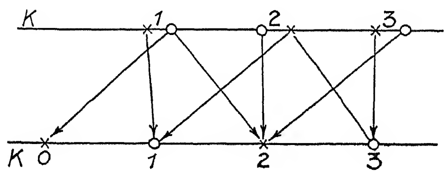


Fig. 4

that the limit of convergence associated with the occurrence of predissociation here corresponds to an Mg atom in the first excited ^2P-state and a normal H atom. For the difference of energy between the convergence limit of $^2\Sigma$ (which is only very roughly known owing to the small number of vibrational levels) and the limit of predissociation nearly corresponds to the first stage of excitation of Mg. Molecules of MgH in a $^2\Sigma$- or $^2\Pi$-state should therefore actually arise from an Mg atom in the ^3P-state and an H atom in the ^2S-state, together with MgH molecules in quartet states which have no bearing on predissociation. The $^2\Sigma$-state is that which we have denoted as $^2\Sigma'$, and has the property of symmetry which we had to assume in order that the lines remaining should be those of the Q-branch. The $^2\Pi$-state, which to avoid confusion with the $^2\Pi$-state hitherto considered we shall denote by $^2\Pi'$, is probably the initial state of the band system which Pearse * denotes by *a*, whose limit of convergence, so far as can be deduced by extrapolation from the few vibrational levels known, also coincides approximately with the limit of predissociation. Obviously $^2\Pi'$ plays merely a subordinate part in the predissociation of the $^2\Pi$-state, for otherwise it would also cause the disappearance of the lines of the Q-branch.

* Pearse, *Proc. Roy. Soc.*, A, **122**, 442 (1929).

In addition to the band $v = 0 \rightarrow v = 0$ Pearse has also investigated the band $v = 1 \rightarrow v = 1$. Here all the rotational levels of the initial state lie above the limit of predissociation, and consequently the P- and R-branches are entirely absent here, so that a Q-branch is alone observed.

A sudden breaking-off of a band has also been observed in the case of AlH by Eriksson and Hulthén * and by Bengtsson and Rydberg.† Here it is a case of a $^1\Pi \rightarrow {}^1\Sigma$ transition. The rotational levels of $^1\Pi$ here seem to become diffuse above the energy value that acts as convergence limit of the $^1\Sigma$-state. Here, however, the lines both of the P- and R-branches and of the Q-branch break off at about the same value of the rotational quantum number. Whether we here have decomposition as a result of rotation or real predissociation cannot be decided with certainty on the basis of the experimental data at present available. The above-mentioned workers also noticed an interesting pressure effect. With a high hydrogen pressure the branches of the bands contain a much higher number of lines than at low pressure. Stenwinkel ‡ has given an explanation of this phenomenon, by indicating that owing to collisions new molecules are always being brought into the states capable of dissociation. Then the number of molecules which radiate before dissociation takes place will be sufficient to give an intensity which can be detected.

According to Mulliken § and Hulthén || a breaking-off of the bands is also observed in CaH. Grundström and Hulthén ¶ have traced out this phenomenon and have also been able to explain it by means of predissociation; a pressure effect similar to that in AlH was also observed.

Finally, we may mention Turner's investigation** of the extinction of the resonance fluorescence of iodine in the magnetic field; he explains this by the assumption that the field sets up the possibility of spontaneous decomposition for the initial state of the emission lines. This can only happen if a selection rule which applies to the

* Eriksson and Hulthén, *Zeitschr. f. Physik*, **34**, 775 (1925).

† Bengtsson and Rydberg, *Zeitschr. f. Physik*, **59**, 540 (1930).

‡ Stenwinkel, *Zeitschr. f. Physik*, **62**, 201 (1930).

§ Mulliken, *Phys. Rev.*, **25**, 509 (1925).

|| Hulthén, *Phys. Rev.*, **29**, 97 (1927).

¶ Grundström and Hulthén, *Nature*, **125**, 634 (1930); Grundström, *Zeitschr. f. Physik*, **69**, 235 (1931).

** Turner, *Zeitschr. f. Physik*, **68**, 178 (1931).

predissociation in the absence of the field is removed by the field; this is probably the rule that J must remain unaltered, for this rule in combination with rules 3 and 5 would make transitions to certain electronic states impossible. In actual fact the magnetic field will destroy the constant character of J if it loosens the coupling of the electronic spin to the line joining the nuclei.

The predissociation of polyatomic molecules, which has chiefly been studied by Henri, would at present seem to be inaccessible to theoretical explanation, as our knowledge of the energy levels of such molecules is still very scanty.

Note.—A more detailed discussion of these and allied phenomena is given in a paper by Herzberg (*Erg. der exakten Naturw.*, **10**, 207 (1931)).

Valency and the Electronic Structure of Molecules

G. HERZBERG, DARMSTADT

A. Introduction

Importance of the Electronic Structure of Molecules.—The cohesion of a molecule depends on the energy of the electrons, whereas the molecular vibrations and rotations which form the chief subject of the previous papers have the effect of loosening the binding. It is only when the electronic energy first decreases as the distance between the two atoms decreases and begins to increase only when the distance between the nuclei is very small that we have a *stable* molecular state. The minimum of the electronic energy (fig. 1) corresponds to the equilibrium position of the two nuclei. To draw theoretical conclusions about the strength of binding in molecular states and hence information about valency we must therefore consider the electronic energy or electronic structure of the molecule.

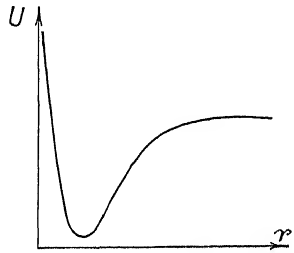


Fig. 1

The modern development of this problem starts from a number of papers by Hund and Mulliken, previous to which and simultaneously with which the experimental material was carefully examined from this point of view, chiefly by Birge and Mecke.

Classification of Electronic Terms.—Here we shall merely give a brief discussion of the notation for the electronic terms of a molecule, as a number of detailed discussions are already available.* The following applies to diatomic molecules only.

As in the case of atoms, the multiplicity of a molecular state is determined by the resultant electronic spin vector† $S = \Sigma s$; it is equal to $2S + 1$

* F. Hund, *Zeitschr. Astrophys.*, **2**, 217 (1931); *Erg. exakt. Naturwiss.*, **8**, 147 (1929): R. S. Mulliken, *Phys. Rev.*, **36**, 611 (1930).

† The angular momentum vectors used here and later are as usual reckoned in terms of units $h/2\pi$. It is also to be noticed, although it is not of importance in what follows, that according to the quantum mechanics the actual vector is not $S \cdot h/2\pi$ but $\sqrt{S(S+1)}\, h/2\pi$.

Hence, just as for atoms, there is an alternation of the multiplicities (Mecke): according as the number of electrons is even or odd, the multiplicity is odd or even.

While the atomic terms are further characterized by the resultant orbital angular momentum L ($L = 0$, S-term; $L = 1$, P-term . . .), the electronic terms of molecules are distinguished by the component Λ of this vector in the direction of the line joining the nuclei. L is no longer a quantum number, as the vector representing the orbital angular momentum executes a rapid precessional motion about the line joining the nuclei owing to the strong electric field in the direction of the latter. As in a magnetic field, it is the component in the direction of the field that is important. Different values of this component correspond to states of different energy; the difference of energy is usually great, so that the states are described as different electronic states. In analogy with the notation for the atomic terms we distinguish between Σ-, Π-, Δ-terms, &c., according as $\Lambda = 0, 1, 2, \ldots$. Terms with $\Lambda > 0$ are doubly degenerate, as in an electric field precession in one direction or the other does not involve a difference of energy.

We accordingly have terms like $^3\Sigma$, $^2\Pi$, $^1\Delta$, &c. Further complications arise from coupling with the rotation of the whole molecule. We shall not discuss these details here, but merely point out that we distinguish between positive and negative rotation terms.* In the case of the Σ-terms the rotational terms are alternatively positive and negative. Then according as the even-numbered ones are positive and the odd-numbered ones negative or vice versa, we distinguish between Σ^+- and Σ^--terms.† In the Π-terms, Δ-terms, &c., we have a positive term and a negative term for each value of the rotational quantum number, owing to the degeneracy; as the rotation increases these terms split up (Λ-doubling).

If the nuclei are identical there is also the symmetry in the nuclei (*ortho* or *para*). The positive rotational terms are symmetrical in the nuclei and the negative ones antisymmetrical; we then speak of even electronic states (e.g. Σ_g, Π_g, &c.): or the negative rotation terms are symmetrical in the nuclei and the positive ones antisymmetrical; we then speak of odd electronic states (e.g. Σ_u, Π_u, &c.). In $\Sigma_g{}^+$-terms (e.g. the fundamental state of H_2), then, the even-numbered rotational terms are symmetrical in the nuclei (*para*-hydrogen), the odd-numbered rotation terms antisymmetrical in the nuclei (*ortho*-hydrogen).

If the nuclei have no angular momentum (spin) of their own, either the rotation states which are symmetrical in the nuclei or those which are antisymmetrical in the nuclei are entirely absent, according as the nuclei are subject to the Fermi statistics or the Bose statistics. If the nuclei possess spin the levels which would be absent if there were no spin do occur but have a smaller statistical weight than the others. A characteristic alternation of intensity is then observed in the bands (Mecke).

If the type of statistics is known we can infer from the nature of this alternation whether the term is even or odd, or conversely if the nature of the term is known we can infer the nature of the statistics to which the nuclei are subject, as was done for N_2 by W. Heitler and the author ‡ (see Rasetti's paper, p. 59).

* According to the symmetry of the ψ-function with respect to reflection in the origin of co-ordinates.

† If there is no rotation they are distinguished by the symmetry of the electronic proper function with respect to a plane passing through the line joining the nuclei.

‡ W. Heitler and G. Herzberg, *Naturwiss.*, **17**, 673 (1929).

B. Theoretical Method of obtaining the Term Manifoldness in Diatomic Molecules

Like the atom, the molecule has a large number of electron terms. The term manifoldness and the term scheme are obtained theoretically as for atoms by decomposing the molecule into its constituent parts and then bringing them together again (building-up principle *). The difference is that in the molecule there are *three* possible methods of synthesis instead of the one in the case of the atom:

1. The term scheme of the molecule may be obtained theoretically and the molecule built up by bringing the atoms of which it consists together, i.e. we investigate the problem what molecular terms arise from definite terms of the separate atoms. If this is carried out for all the possible combinations of atomic terms, we obtain the whole set of terms of the molecule.

2. The term manifoldness may be obtained by starting with the nuclei at zero distance apart instead of infinite distance, i.e. by *splitting up the "united atom"*. This procedure, of course, is quite hypothetical, but may nevertheless be used to determine the term manifoldness.

3. Finally, we may use the exact analogy of the method employed for atoms, i.e. adding the *single electrons successively* to the free nuclei and seeing in what orbits or quantum cells they arrange themselves. The possible types of arrangement then give the possible terms, as in the atom.

1. *Determination of the Term Manifoldness from the Terms of the Separate Atoms.*—Hund † and Wigner and Witmer ‡ have given the complete theoretical rules for determining what molecular terms arise from definite atomic terms in the case of diatomic molecules. These rules are best explained by means of the vector model. For the case of slight multiplet splitting, where the interaction between S and L may be neglected, we have merely to combine the S-vectors of the separate atoms vectorially according to the quantum mechanics. The resultant spin vector of the molecule is $S = S_1 + S_2,\ S_1 + S_2 - 1,\ \ldots\ |S_1 - S_2|$. The orbital angular momentum vectors L_1, L_2, on the contrary, are quantized spatially as the atoms approach one another with respect

* Ger. *Aufbauprinzip*.

† F. Hund, *Zeitschr. f. Physik*, **42**, 93 (1927).

‡ E. Wigner and E. E. Witmer, *Zeitschr. f. Physik*, **51**, 859 (1928).

to the line joining the nuclei. In order to obtain the Λ-value of the resulting molecular term we have to add the components of L_1 and L_2. According to the value of these components, i.e. according to the direction of the L-vectors of the separate atoms, various Λ-values, i.e. various molecular states, arise from the same atomic states. Here we must bear in mind that terms for which $\Lambda > 0$ arise in two ways differing only in sign. Each of the Λ-values thus obtained may have any of the values of the manifoldness which follow from the above S-values.

From these rules it follows, for example, that from an atom in the ^{2}D-state (e.g. excited N) and an atom in the ^{3}P-state (e.g. normal O), we obtain one $^2\Phi$-term, two $^2\Delta$-terms, three $^2\Pi$-terms, three $^2\Sigma$-terms, and an equal number of quartet terms, i.e. 18 different molecular terms in all. If one of the atoms is in an S-state and the other in a P-state, only Σ- and Π-terms result; e.g. for $^4S + {}^3P$ (N + O in the fundamental state) we get $^2\Pi$, $^2\Sigma$, $^4\Pi$, $^4\Sigma$, $^6\Pi$, $^6\Sigma$.

If the two atoms (or ions) have *identical nuclei* and are not in the same state, just twice as many molecular states result. Each of the above states occurs once as an even term and once as an odd term. This is due to resonance degeneracy; when the atoms are brought together, the one atom may for example be normal and the other excited or ionized, or conversely.

Thus e.g. an O atom (^{3}P) and an O^+ ion (^{4}S) give rise to twice as many terms as do N and O (see above), although in both cases we have $^3P + {}^4S$; besides others, O_2^+ therefore has *two* $^2\Pi$-terms, as seems actually to be observed.*

If the two atoms with identical nuclei are in the same state this resonance degeneracy naturally does not occur, and there are exactly as many terms as when the nuclei are different, except that the terms are alternately even and odd.† Here we shall merely mention that in this way it is theoretically found that two normal N atoms give the terms $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^5\Sigma_g^+$, $^7\Sigma_u^+$. The fundamental state is $^1\Sigma_g^+$. From the observed alternation of intensity (the odd-numbered rotational levels are feebler than the even-numbered) we deduce the Bose statistics for the N nuclei.‡

In a similar way we obtain a result which has become of great importance in chemistry, namely that normal O atoms give rise to three such $^3\Sigma$-terms, which according to the selection rules cannot combine with one another ($^3\Sigma_u^-$, $^3\Sigma_u^-$, $^3\Sigma_g^+$), i.e. that the higher state of the ultra-violet O_2 bands

* G. Herzberg, *Zeitschr. f. Physik*, **57**, 601 (1929).

† For a more accurate discussion see F. Hund, *Zeitschr. f. Physik*, **63**, 719 (1930).

‡ W. Heitler and G. Herzberg, *Naturwiss.*, **17**, 673 (1929).

must, unlike the fundamental state, arise from one normal and one *excited* oxygen atom, so that the heat of dissociation of O_2 falls short of the energy corresponding to the point of convergence (7·0 volts) by this excitation energy, amounting to 1·9 volt.*

2. *Determination of the Term Manifoldness from the Terms of the United Atom.*—The Λ-values for the molecular terms arising from a definite term of the *united atom* are simply the components of the corresponding value of L in the electric field which arises from the separation of the nucleus, the degeneracy for $\Lambda > 0$ again being borne in mind. Thus a D-term of the united atom gives rise to a Σ-term, a Π-term, and a Δ-term. The multiplicity remains the same. More detailed statements as to when Σ^+- and Σ^-- and when even and odd terms arise are given in the paper by Hund referred to on the opposite page.

3. *Determination of the Term Manifoldness from the Electronic Configuration.*—This third method was first applied to molecules by Mulliken † and Hund.‡ It is entirely analogous to the method for atoms. The only difference is that the nuclei must be held *fixed*, as in the absence of electrons they would of course fly apart. Thus what we discuss is a *system of two centres of force*, which serves as a molecular model. In the first instance nothing is said as to how the nuclei (which of course are really *free*) move under the influence of the maintained electronic configuration or whether they attract or repel one another.

The essential advantage of this method is that it immediately explains the fundamental fact that *different molecules with the same number of electrons have very similar physical properties*, although they are made up of quite different atoms or atomic terms. For if the nuclei do not differ too greatly, the term scheme depends on the number of electrons only, just as in the case of atoms (e.g. Li, Be^+, B^{++}, &c.), as the electrons then have the same quantum numbers (see further below), which is independent of the nature of the nuclei. This very similarity is impossible of explanation on the basis of the first method, for it starts from the separate atoms. Thus e.g. CO and N_2 exhibit a very striking similarity in their physical properties (melting-point, boiling-point, &c.). Both have a $^1\Sigma^+$-state as fundamental state. In particular, the far-reaching similarity between the curves of effective cross-section with respect

* See G. Herzberg, *Zeitschr. f. phys. Chemie*, B, **4**, 223 (1929); **10**, 189 (1930).

† R. S. Mulliken, *Phys. Rev.*, **32**, 186, 761 (1928).

‡ F. Hund, *Zeitschr. f. Physik*, **51**, 759 (1928).

to slow electrons * is strong evidence for their having the same electronic configuration in the fundamental state (each has 14 electrons). Spectroscopically a number of molecules with 13 electrons are known (CN, N_2^+, BO, CO^+). Qualitatively they all exhibit the same term diagram (a low $^2\Sigma$-term, a $^2\Pi$-term, and a $^2\Sigma$-term). For the same reasons we may accordingly expect a similarity between the two molecules BN and C_2 with 12 electrons also. Unfortunately BN has not yet been investigated spectroscopically. It is remarkable, however, that these two molecules, and they alone, crystallize according to the graphite lattice. This probably indicates a similarity in the valency properties of the C_2 and BN molecules, which is also to be anticipated from the above considerations.

N_2 arises from two ^4S nitrogen atoms, which give four terms in all ($^1\Sigma$, $^3\Sigma$, $^5\Sigma$, $^7\Sigma$); CO arises from ^3P(C) and ^3P(O), which give 18 different terms in all (one each of $^1\Delta$, $^3\Delta$, $^5\Delta$, two each of $^1\Pi$, $^3\Pi$, $^5\Pi$, and three each of $^1\Sigma$, $^3\Sigma$, $^5\Sigma$). How the agreement between the fundamental states arises cannot therefore be seen at all from the first method, just as in the other cases, unless the calculation is carried to a very high degree of approximation.

In order to carry out this building-up principle for the electrons in the molecule or system of two centres of force, we must ascribe quantum numbers to the *individual electrons* in the molecule; these, of course, are different from those in the atom, just as the quantum numbers characterizing the whole term are. As in the atom, we can only introduce these quantum numbers by neglecting the mutual action of the electrons to a certain extent, i.e. by investigating the motion of each electron in the field of the others, which spreads out symmetrically with respect to an axis.

In concrete language, then, the component λ of the orbital angular momentum in the direction of the line joining the nuclei is essential for the characterization of the state of an electron. According as $\lambda = 0, 1, 2, \ldots$, we distinguish σ-, π-, δ- ... electrons. If the nuclei are identical or nearly identical, we have also to distinguish between even and odd electrons, according to the symmetry of the proper functions with respect to the plane which normally bisects the line joining the nuclei. We accordingly have σ_g-, σ_u-, π_g-, π_u-, ... electrons. The quantum number λ fully corresponds to the quantum number m_l of the electrons in an atom. It follows at once that in virtue of the Pauli principle there can only be *two* equivalent σ-electrons, but *four* equivalent π-, δ-, &c., electrons,

* E. Brüche, *Naturwiss.*, **17**, 252 (1929).

since for $\lambda > 0$ the rotation can of course take place in one direction or the other about the line joining the nuclei (corresponding e.g. to $m_l = \pm 1$).

In general, of course, these quantum numbers are insufficient to characterize an electron completely. To distinguish non-equivalent electrons two different methods have been proposed.

1. We may also add those quantum numbers which the electron in question would have in the *united atom* if the whole transition took place neglecting the interaction of the electrons (as above). This method of characterization is due to Mulliken and Hund. If the nuclei are sufficiently close together, the various electronic shells succeed one another in the same way as in the united atom, except that the quantization in the electric field of the nuclei has to be taken into consideration. In addition to the well-known scheme according to which the shells of atoms are built up, Table I (p. 162) gives the quantum numbers of the united atom, and below them those of the molecule with the two nuclei very close together. The *s*-electrons become σ-electrons ($1s\sigma$, $2s\sigma$, . . .). Of the *p*-electrons those for which $m_l = 0$ become σ-electrons ($2p\sigma$, &c.), those for which $m_l = \pm 1$ become π-electrons, and so on. The $p\sigma$-electrons, as Hund has shown, lie lower as regards energy than the $p\pi$-electrons. If the nuclei are identical or nearly identical, the electrons for which l is even in the united atom become "even" electrons in the molecule ($s\sigma$, $d\sigma \rightarrow \sigma_g$, $d\pi \rightarrow \pi_g$, &c.), and those for which l is odd become "odd" electrons ($p\sigma$, $f\sigma \rightarrow \sigma_u$, $p\pi$, $f\pi \rightarrow \pi_u$, &c.). The succession in the molecule of course usually differs from that given in the table. We see, however, that in a molecule like N_2 the two pairs of K-electrons in this diagram cannot have the same quantum numbers, although they certainly have almost the same energy.

2. To avoid this Lennard-Jones * and later Dunkel † have taken into consideration the quantum numbers which the electrons would have in the *separate atoms*, e.g. $\sigma_u(2s)$, $\pi_g(2p)$, &c.‡ In theory, of course, both methods come to the same thing. Which method one selects in a particular case is merely a question of convenience.

Knowing the succession of the various electronic shells in the molecule we can theoretically deduce the *term scheme*, just as

* J. E. Lennard-Jones, *Trans. Farad. Soc.*, **25**, 668 (1929).

† M. Dunkel, *Zeitschr. f. phys. Chemie*, B, **7**, 81 (1930).

‡ Cf. Hund, *Zeitschr. f. Physik*, **63**, 719 (1930).

TABLE I

	K	L				M								
n	1	2				3								
l	0	0	1			0	1			2				
m_l	0	0	0	+1	−1	0	0	+1	−1	0	+1	−1	+2	−2
m_s	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
Quantum numbers of the electrons in the atom.	$1s^2$	$2s^2$	$2p^6$			$3s^2$	$3p^6$			$3d^{10}$				
Quantum numbers of the electrons in the molecule.	$1s\sigma^2$	$2s\sigma^2$	$2p\sigma^2$	$2p\pi^4$		$3s\sigma^2$	$3p\sigma^2$	$3p\pi^4$		$3d\sigma^2$	$3d\pi^4$		$3d\delta^4$	

in the case of atoms. The lowest term is that for which each electron is in the lowest possible orbit. Higher terms are obtained by bringing the most loosely bound electron into a higher "orbit", or, as appears to occur frequently in molecules, bringing inner electrons into outer orbits. As in atoms, *closed shells* always give $^1\Sigma$-terms ($S = \Sigma s = 0$, $\Lambda = \Sigma\lambda = 0$), i.e. they may be neglected in determining the nature of the term. A single σ-electron outside closed shells gives a $^2\Sigma$-term, a single π-electron a $^2\Pi$-term. Two non-equivalent σ-electrons give a $^1\Sigma$-term and a $^3\Sigma$-term; the two spins may be parallel or antiparallel to one another. Two

TABLE II

Electronic Configuration	Terms
$(A)\sigma$	$^2\Sigma$
$(A)\pi$	$^2\Pi$
$(A)\sigma\sigma$	$^1\Sigma^+$, $^3\Sigma^+$
$(A)\sigma\pi$	$^1\Pi$, $^3\Pi$
$(A)\pi^2$	$^1\Sigma^+$, $^1\Delta$, $^3\Sigma^-$
$(A)\pi\pi$	$^1\Sigma^+$, $^3\Sigma^+$, $^1\Sigma^-$, $^3\Sigma^-$, $^1\Delta$, $^3\Delta$

(A) denotes closed shells

equivalent π-electrons may have either parallel orbital angular momenta λ, when the spins must be antiparallel, i.e. $^1\Delta$. $^3\Delta$ is not possible; or antiparallel orbital angular momenta (i.e. $\Lambda = \Sigma\lambda = 0$), when the spins may be either parallel or antiparallel, i.e. there is a $^3\Sigma$-term and a $^1\Sigma$-term. As in the case of atoms, we expect that of these three terms of the same electronic configuration π^2 the term of greatest multiplicity, i.e. $^3\Sigma$, will lie lowest. These cases, together with some others, are summarized in Table II.* Whether the resulting terms are even or odd in the case of homonuclear molecules depends on whether the number of odd electrons (see above) is even or odd.

* Taken from a more extensive table in a paper by Hund (*Zeitschr. f. Physik*, 63, 719 (1930)).

C. Correlation and Stability of the Molecular Terms

All the three methods for determining the term manifoldness discussed in the previous section must of course give the *same* terms for a definite internuclear distance, and in the same order and position. This, however, can only be accurately tested if the calculation is carried to high approximations, as methods (1) and (2) in particular start from a state which is no proper approximation to the molecule. Without these more exact calculations the above methods give the term manifoldness only, and in the case of (3) the approximate succession of terms also. As regards the *stability* of the molecular terms thus found, i.e. whether the corresponding potential curve has a minimum or not, nothing is as yet revealed. In method (3), in particular, the nuclei are held fixed (system of two centres of force), so that nothing is said in the first instance about their behaviour when let loose. The question of stability, however, is the very thing that interests the spectroscopist and the chemist, for the molecular states which they observe are of course stable molecular states in general, and they are interested in the question how it is that the observed molecular state is stable, and why other molecular states which could theoretically occur are unstable (having no minimum in the potential curve) and hence are not observed. In addition, the answer to the question into what atomic state the molecular state dissociates, i.e. the question of the correlation of the molecular terms with those of the separate atoms, is of importance. Only when it is answered will it be possible to make reliable statements about the processes of dissociation and heats of dissociation (cf. Miss Sponer's paper, p. 97); this has been shown * e.g. in the determination of the heat of dissociation of O_2.

The Method of Heitler and London.—In order to answer the question of the stability of the molecular states which are theoretically possible, Heitler and London, as is well known, have carried out a calculation † on the basis of quantum mechanics, starting from the state where the nuclei are very far apart as an approximation of zero order, i.e. using method (1). For atoms which are in S-states, they thus obtained a simple physical result, namely, that the Σ-states obtained lie as regards energy in the order of their multiplicity, i.e. the $^1\Sigma$-state is the lowest. This $^1\Sigma$-state, then, is a stable

* G. Herzberg, *Zeitschr. f. phys. Chemie*, B, **4**, 223 (1929); **10**, 189 (1930).

† W. Heitler, *Phys. Zeitschr.*, **31**, 185 (1930).

molecular state, if the separate atoms were not in ^{1}S-states. In this way Heitler and London were led to the well-known ideas of the nature of the mechanism of valency and saturation, ideas which are in fact very simple and intuitive. The method, however, suffers from the disadvantage that whenever one or both of the atoms is in a P-state (or L exceeds zero at all) very complicated results are obtained, which have only just been worked out accurately.* Hitherto it has not been possible to set up any rules of general applicability.

The Method of Electronic Configuration.—It is therefore not superfluous to attack the problem from quite another angle by using the method of electronic configuration (method (3)) as developed by Mulliken and Hund. This method actually gives the approximate succession of the various electronic terms in the molecule (see further below). To begin with, the main thing is to establish which of the molecular terms obtained from the terms of the separate atoms correspond to these, i.e. what is the relationship between the molecular terms resulting from the electronic configuration and the terms of the separate atoms. If this relationship is known the stability of the resulting molecular terms is in many cases also known. If e.g. three molecular terms are related to two atomic terms in the way shown in fig. 2, we may infer that the uppermost molecular term will be unstable, as it lies higher in the molecule than another term which has resulted from a more highly excited state of the separate atoms.

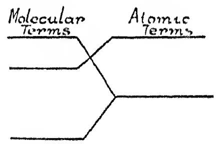


Fig. 2

The method of electronic configuration also has the advantage that the case where the separate atoms are in P-states can be considered at the same time without more ado (see further below).

Succession of the Electronic Shells for various Internuclear Distances.—To obtain the correlation of terms we first attempt to obtain the succession of the various electronic shells for all possible internuclear distances. For the two extreme cases ($r = 0$ and ∞) it may be obtained theoretically when the nuclei are identical or nearly identical, as has been shown by Hund.† In the following diagram (fig. 3) these two successions are given on the left and on the right. The left-hand column agrees with the lowest row of

* W. Heitler, *Phys. Zeitschr.*, **31**, 185 (1930); J. H. Bartlett, *Phys. Rev.*, **37** 507 (1931); and others.

† F. Hund, *Zeitschr. f. Physik*, **51**, 759 (1928); **63**, 719 (1930).

Table I (p. 162). The right-hand column is obtained in the following way: if the nuclei are far apart and there is a single $1s$-electron, this becomes a σ-electron, and owing to the degeneracy arising from the fact that the electron can be at either nucleus (with the same energy), the associated proper function is either even or odd; the electron becomes σ_g or σ_u, σ_g lying deeper than σ_u as the nuclei approach. If the nuclei are far apart and there are several $1s$-electrons (at most

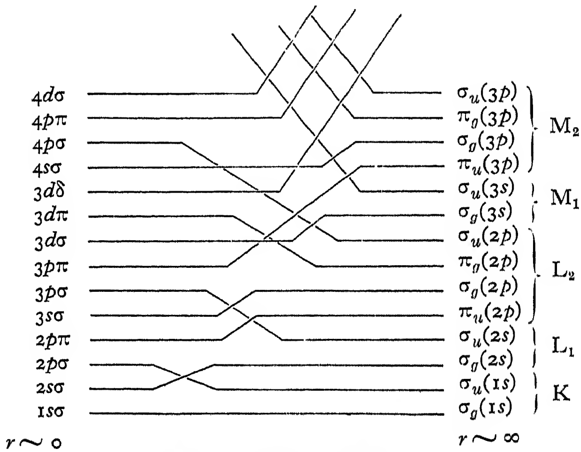


Fig 3.—Correlation Diagram

4, of course), these become either $\sigma_g(1s)$ or $\sigma_u(1s)$. Similarly for the $2s$-electrons. The $2p$-electrons can become either σ-electrons or π-electrons and again either even or odd. According to Hund the succession is as given above. Similar considerations apply to the other orbits.

The succession of the various electronic shells in the actual molecule must lie between these two limiting cases. We may assume that the transition between the two limiting cases takes place with as few changes in the order of succession as possible. The lines drawn in fig. 3 * between the electronic shells for the two limiting cases represent a plausible variation of the succession with the internuclear distance.† This diagram enables us to determine the

* Of course the associated electrons joined must always be of the same type, i.e. σ_g and σ_g, π_u and π_u, &c. In the notation for the united atom (on the left) those electrons, as mentioned above, are even for which l is even and those are odd for which l is odd.

† In the higher shells the change in the order of succession takes place at a greater internuclear distance than for the lower shells, because when two atoms

possible electronic configurations for any internuclear distance, and hence the order of succession of the electronic terms.

The Correlation Rules.—The question now arises how the terms arising for the various internuclear distances are to be correlated. Hund previously believed* that this had to take place in such a way that as few crossings as possible occur. According to this, for example, the $^1\Sigma_g{}^+$-term, which arises from two normal He atoms and is formed by the electronic configuration $\sigma_g{}^2\sigma_u{}^2$ when the nuclei are far apart, would when the nuclei are close together be represented by the lowest electronic configuration resulting in a $^1\Sigma_g{}^+$-term, i.e. by $\sigma_g{}^2\sigma_g{}^2$ or $1s\sigma^2 2s\sigma^2$, and similarly in similar cases. The author † then proposed another classification rule, namely that *terms with the same electronic configuration are to be classified together.* In the above-mentioned example the $\sigma_g\sigma_u{}^2\,{}^1\Sigma$-term of He_2 with the nuclei far apart would accordingly be associated with the $\sigma_g{}^2\sigma_u{}^2\,{}^1\Sigma_g{}^+$-term with the nuclei close together, i.e. with a term which when the nuclei are close together lies very high. This rule appears to be better supported by the experimental material,‡ and the assumption also enables a simple interpretation of the idea of the *valency of a bond* to be given.

Conclusions as to Stability.—The above-mentioned correlation rule enables us to tell which electrons of the separate atoms give rise to each electronic shell in the complete molecule. It also follows that the changes in energy as the nuclei approach one another can be simply determined by investigating whether the energy of each separate electronic shell is decreased or increased. To a first approximation the change in energy of the whole system is then regarded as given by the superposition of these separate energy changes.§ This method, of course, is only a very approximate one, for, as we said above, the interaction of the electrons is to a certain extent neglected. As has been emphasized especially by Weizel || and later by Hund, ¶

are brought together the outer shells are obviously the first to re-group themselves and the inner shells the last. In a molecule like N_2, for example, the K-shells have practically the same energy as in the separate atoms, so that in their case no change in the succession can have occurred, in contradistinction to the L-shells.

* *Zeitschr. f. Physik*, **51**, 759 (1928).

† G. Herzberg, *Zeitschr. f. Physik*, **57**, 601 (1929).

‡ See Herzberg, loc. cit., and Hund, *Zeitschr. f. Physik*, **63**, 719 (1930).

§ Cf. R. S. Mulliken, *Phys. Rev.*, **32**, 186, 761 (1928).

|| W. Weizel, *Zeitschr. f. Physik*, **59**, 320 (1930).

¶ F. Hund, *Zeitschr. f. Physik*, **63**, 719 (1930).

the method is only justifiable so long as the quantum properties defined by the quantum numbers of the individual electrons are definable all the way from large values of r to small values. Whether this condition is satisfied must be settled in each case on the basis of the experimental data.

Binding and Loosening Electrons.—The great advantage of this method is that as the potential curve of the whole molecule is obtained so as to speak by superposition of the potential curves for each electron, we can now distinguish between binding electrons and loosening electrons * in the same way as is obviously possible in the system of two nuclei with one electron † (H_2^+). Binding electrons are those which make a positive contribution to the strength of binding, loosening electrons those which make a negative contribution.‡ The last holds particularly for those electrons which according to the above diagram move up when the nuclei come closer together. The loosening effect of these electrons will be particularly large for those internuclear distances for which the crossing has already taken place (for then those electrons which arise from electrons lying much higher in the separate atoms lie lower as regards energy), but will also appear for internuclear distances which are somewhat greater.§

As we shall see below, the distinction between binding electrons and loosening electrons in the method of electronic configuration (method (3)) leads, on the one hand, to an explanation, based on this method, of the Heitler-London theory, which at first sight

* Cf. G. Herzberg, *Zeitschr. f. Physik*, **57**, 601 (1929), and F. Hund, *Zeitschr. f. Physik*, **63**, 719 (1930).

† Cf. the theoretical potential curves of Morse and Stueckelberg (*Phys. Rev.*, **33**, 932 (1929)), Lennard-Jones (*Trans. Farad. Soc.*, **25**, 668 (1929)), and Teller (*Zeitschr. f. Physik*, **61**, 458 (1930)).

‡ Cf. also R. S. Mulliken, *Phys. Rev.*, **32**, 186, 761 (1928).

§ "Loosening electrons" in the above sense are not always "promoted electrons in Mulliken's sense. Mulliken's "promotion" consists in the fact that when two atoms combine to form a molecule the principal quantum numbers of some of the electrons must be raised even when the nuclei are far apart, if the electrons are denoted by their quantum numbers in the united atom. Here the loosening effect arises from the fact that when the atoms are brought together some electronic shells rise higher than others which lie higher when the nuclei are far apart. If there were no crossing-over, there would be no loosening electrons in the above sense, but the number of Mulliken's "promoted electrons" would remain unchanged. For example, the $\sigma_g(2p)$ electrons become $3s\sigma$ in the united atom, *i.e.* are promoted in Mulliken's sense. Here, however, they are to be regarded as binding electrons. Mulliken himself (loc. cit.) has already pointed out that promoted electrons can sometimes have a binding effect also.

seemed quite unattainable.* On the other hand, when the atoms are in P-states, it also leads, as was mentioned above, to simple results which are in agreement with experiment but which were not immediately intelligible on the simple Heitler-London valency theory.

The simple rule which we take as our basis is that a stable molecular state is only to be expected if *the number of binding electrons exceeds the number of loosening electrons*.†

It will appear that the number of pairs of binding electrons minus the number of pairs of loosening electrons gives the *valency of a bond* directly. This will best be illustrated by means of the examples discussed below.

Examples.‡—H_2^+ and H_2. In the case of H_2^+, as Teller § and others have shown by means of strict quantum-mechanical calculations, the one $\sigma_g(1s)$ or $1s\sigma$-electron gives fairly strong binding (heat of dissociation 2·7 volts, binding electron), while the $\sigma_u(1s)$ or $2p\sigma$-electron, whose proper function has a node in the median plane, gives practically repulsion only (loosening electron). Here it is important to note that a single electron can give rise to firm binding without any pair-formation in the Heitler-London sense being necessary. If in $H + H$ the two electrons become $\sigma_g(1s)$-electrons, we may expect the binding to be stronger than in H_2^+, and this is actually observed. The two electrons can then become $\sigma_g(1s)$-electrons only when the spins are antiparallel, i.e. for the $^1\Sigma$-state. If they have parallel spins, they must be in different electronic shells, i.e. $\sigma_g(1s)\sigma_u(1s)\,^3\Sigma$. In this case, then, we have a binding electron and a loosening electron, i.e. no binding is to be anticipated. In both cases, therefore, there is agreement with the results of Heitler and London, but without any need to make use of " exchange forces ".

When the nuclei are far apart the H_2 term $1s\sigma\,2s\sigma$ or $\sigma_g(1s)\,\sigma_u(2s)$ lies about 10 volts above the fundamental state. As when the

* Cf. Mulliken, *Phys. Rev.*, **32**, 186, 761 (1928).

† G. Herzberg, *Zeitschr. f. Physik*, **57**, 601 (1929); F. Hund, *Zeitschr. f. Physik*, **63**, 719 (1930). We may expect that a binding electron and a loosening electron will compensate each other only when they arise from the same shells of the separate atoms. Even then, of course, the rule is only a rough approximation.

‡ In what follows the fundamental states of the molecules are discussed for the most part. The excited states may also be dealt with by this method; see F. Hund, *Zeitschr. f. Physik*, **63**, 719 (1930).

§ E. Teller, *Zeitschr. f. Physik*, **61**, 458 (1930).

nuclei are close together the state $1s\sigma\, 2p\sigma$ lies higher, and still does so for an internuclear distance which is only slightly less than that for the stable molecule,* it likewise follows that the term $1s\sigma\, 2p\sigma\, {}^3\Sigma$ must be a repulsion term.† The more highly excited states of H_2 may be dealt with in a similar way. We must, however, take note of the fact that no symmetry remains when $r = \infty$. Hund (loc. cit.) has worked out the details.

He_2. In He_2 in the fundamental state we have one pair of binding electrons and one pair of loosening electrons, $\sigma_g^2(1s)\,\sigma_u^2(1s)$ or $1s\sigma^2\, 2p\sigma^2$, i.e. no binding. When the nuclei are close together the repulsion in this case is particularly strong, because the state resulting from normal atoms then lies higher than that arising from two excited helium atoms, and the latter lies 40 volts above the fundamental state when the nuclei are far apart (cf. fig. 2). If He and He^+ are brought together we have only one loosening electron and two binding electrons. Binding is therefore possible; this is in agreement with the experimental results of Weizel.‡ In addition there is the polarizing effect of He^+ on He. Similar results follow when a normal He atom and an excited He atom are brought together. Binding is then possible provided the excited electron is not a loosening electron. The lowest state which can arise in this way is $1s\sigma^2\, 2p\sigma\, 2s\sigma$ (*one* resultant pair of binding electrons).

Li_2. When the nuclei are far apart the lowest state of Li_2 is obviously $\sigma_g{}^2\sigma_u{}^2\sigma_g{}^2\, {}^1\Sigma_g{}^+$; we therefore have two pairs of binding electrons and one pair of loosening electrons, i.e. one resultant pair of binding electrons, so that a stable molecular state is possible. The fact that the strength of binding is not very great (1·14 volts, according to Loomis and Nusbaum §) may be connected with the fact that the principal quantum number of the binding electrons exceeds that of the binding electrons of H_2 by one. ||

Be_2. In Be_2, as in He_2, no stable state may be expected to arise

* See Hund, loc. cit.

† The states $\sigma_u^2(1s)\, {}^1\Sigma$ and $\sigma_g(1s)\,\sigma_u(1s)\, {}^1\Sigma$ also arise from K-electrons of the separate atoms and in fact correspond to dissociation into ions ($H^+ + H^-$). From the above diagram it is not obvious that this state lies about 13 volts above the fundamental state, as is actually the case. This is due to the fact that we neglected the interaction of the electrons. Hund (loc. cit.) has attempted to overcome the difficulties involved in this.

‡ W. Weizel, *Zeitschr. f. Physik*, **59**, 320 (1930).

§ F. W. Loomis and R. E. Nusbaum, *Phys. Rev.*, **37**, 1712 (1931).

|| Cf. M. Delbrück, *Ann. d. Physik* (5), **5**, 36 (1930).

from normal atoms, but such may arise from a normal atom and an excited atom. Be_2 bands have not yet been detected experimentally.

B_2, again, should be capable of forming a stable molecule. The molecular state resulting from normal atoms, however, like that of Li_2, should not exhibit great strength of binding. This will, however, be the case for a state which arises from two excited atoms (lowest quartet state), quite in agreement with the results of Heitler and London (triple bond, three pairs of binding electrons).

C_2. Similar results hold in this case. There is a double bond and a quadruple bond. Unfortunately the experimental data in this case as in many others are not nearly adequate for definite conclusions to be reached.

N_2. Two normal N atoms with the nuclei far apart form the configuration $\sigma_g{}^2\sigma_u{}^2\sigma_g{}^2\sigma_u{}^2\pi_u{}^4\sigma_g{}^2\,{}^1\Sigma$, i.e. there are three resultant pairs of binding electrons (cf. fig. 3); in agreement with chemical ideas of valency, the bond is to be regarded as triple. The characteristic feature of the fundamental state of N_2 is that in its formation from the separate normal atoms, as in the formation from the normal united atom, none of the electronic shells lead to excited states, no matter what the distance between the nuclei, and all the shells are complete. It is to this that the resemblance between N_2 and the inert gases is apparently due. Moreover, the first excitation potential is very high (8·3 volts) because the following shell is a loosening shell.* This high resonance potential is also a characteristic of the inert gases.

O_2. The two extra electrons which O_2 has as compared with N_2 become $\pi_g(2p)$-electrons, i.e. loosening electrons. The binding of the fundamental state of O_2 is therefore less strong than that of N_2, as has been observed ($3 - 1 =$ double bond). According to what we have said above, two equivalent π-electrons can give three different terms, ${}^3\Sigma$, ${}^1\Sigma$, and ${}^1\Delta$, of which the ${}^3\Sigma$-term lies lowest. The fundamental state of O_2 accordingly turns out to be ${}^3\Sigma$, in agreement with experiment. This fact contradicts the simple Heitler-London theory, according to which the saturation of the valencies depends on the saturation of the spins. We conclude rather that this saturation of the spins has less effect on the valency of a bond than the excess of binding electrons over loosening electrons, and we accordingly ascribe a double bond to the O_2 molecule, in agreement

* The possibility of drawing a conclusion about the magnitude of the excitation potential indicates a further advantage of the method used here.

with the usual chemical ideas of valency, in spite of its $^3\Sigma$ fundamental state.

F_2. In F_2 there are two more loosening electrons. Here, therefore, we have a single bond. The fundamental state is $^1\Sigma$, as the π-shell is now complete.

Ne. When two Ne atoms are brought together, half of the electrons are binding, half loosening, as in all cases of atoms with closed shells only. A stable molecule is therefore impossible.

In Na_2, P_2, S_2, Cl_2 the relationships recur exactly as in the cases discussed, except that the principal quantum numbers are correspondingly increased and the energy relationships are therefore different.

Application to Molecules with Two Different Nuclei.—As was mentioned above, the above considerations really hold only for homonuclear diatomic molecules. They may, however, be also applied to cases where the two nuclei do not differ too greatly. In connexion with what Mecke has said in his paper (p. 34) we may here mention NO, in which there are three pairs of binding electrons and one loosening electron ($\pi_g[2p]$) in the fundamental state. By excitation this loosening electron may be made into a binding electron ($\sigma_g[3s]$) and then, as is actually found, we obtain a state of very great binding strength, which (again in agreement with experiment) should dissociate into atoms, in one of which one electron is in the M-shell ($n = 3$).*

With suitable modifications even the hydrides may be considered.† Here it is very probable that the electron of the normal H atom will always become a σ electron of the molecule. As examples we shall consider BH and CH, as they are important in what follows. The ^{2}P-term of the B atom gives a $\sigma^2\sigma^2\sigma\,^2\Sigma$- or $\sigma^2\sigma^2\pi\,^2\Pi$-state in the electric field due to the approach of the H atom. By addition of a σ-electron we therefore obtain $\sigma^2\sigma^2\sigma^2\,^1\Sigma$ as the lowest state (fundamental state) of BH, in accordance with the order of succession in the left-hand column of the diagram above (p. 166), which always holds for hydrides in view of their small internuclear distance. The following states also arising from normal atoms are $\sigma^2\sigma^2\sigma\pi\,^1\Pi$ and $^3\Pi$. A $^1\Pi \rightarrow {}^1\Sigma$ transition in BH has recently been discovered by Lochte-Holtgreven and Vleugel.‡ The fundamental

* Cf. R. S. Mulliken, *Phys. Rev.*, **32**, 186, 761 (1928), and G. Herzberg, *Zeitschr. f. Physik*, **57**, 601 (1929).

† Cf. R. S. Mulliken, *Phys. Rev.*, **33**, 730 (1929).

‡ W. Lochte-Holtgreven and E. S. van der Vleugel, *Zeitschr. f. Physik*, **70**, 188 (1931).

state of C, ^3P, gives $\sigma^2\sigma^2\sigma\pi\ ^3\Pi$ and $\sigma^2\sigma^2\pi^2\ ^3\Sigma$ in the electric field. By addition of a σ-electron the former becomes the lowest observed state of CH, $^2\Pi$. The $^3\Sigma$-state of the atom in the electric field gives as lowest state a $\sigma^2\sigma^2\sigma\pi^2\ ^4\Sigma$-term, which might very well lie below the $^2\Pi$-term. Experimentally, however, it has not been observed as yet. If really stable it would, as will appear below, contradict the Heitler-London idea that a pair of electrons with antiparallel directions of spin must be formed in order to bind a hydrogen atom to the carbon atom. As well as other states, an excited $^2\Delta$-state of CH has also been observed. This can only have arisen from a carbon atom in the ^1D-state, the electronic configuration being again $\sigma^2\sigma^2\sigma\pi^2$. The fact that this state is stable is worthy of note because the carbon atom is in a singlet-state, i.e. should not, according to the original Heitler-London ideas, enter into any binding with a hydrogen atom.* Both cases show that the nature of the terms or the number of electrons not forming pairs is not so important as the electronic configuration. *Different* atomic terms with the *same* electronic configuration, which can give molecular terms of the same electronic configuration when the nuclei are far apart, will in general all give repulsion or all attraction. This very fact seems to us to have an important bearing on the explanation of the failure of the Heitler-London theory in certain cases, for it takes into account only the nature of the resultant term of the separate atoms, not, as here, the electronic configuration.

General Conclusions.—From what we have said above, there is a degree of agreement, which we consider very satisfactory, between the results of the method of electronic configuration (method 3) and those of experiment. The underlying assumptions thereby

* Cf. Mulliken, *Phys. Rev.*, **32**, 186, 761 (1928). Similarly, according to Heitler and London, the atoms in the second column of the periodic table, Be . . . Hg, which have a ^1S-state as fundamental state, should be incapable of forming a true valency bond with hydrogen. They ascribe the binding strength which is actually observed and which in some cases is considerable to polarization forces. In the light of what we have said above, the binding in this case is quite intelligible, as a binding electron is present, and it is not necessary to assume a special type of binding. Here again the nature of the terms and the possibility of the formation of pairs of electrons with antiparallel directions of spin do not seem to be so important as the electronic configuration and the excess of binding electrons over loosening electrons. Also of great importance in this connexion is the fact, quite recently deduced from band spectra by Mulliken and Christy (*Phys. Rev.*, **38**, 87 (1931)), that even in the fundamental state of HgH, which has a binding strength of only 0·37 volts, the electronic configuration is very like that of the united atom and not, as would be anticipated if the bond were assumed to be a polarization bond, like that of the separate atoms.

seem to have gained support, in particular the physical idea that the strength of a bond, or the possibility of its being formed at all, depends on the *excess of binding electrons over loosening electrons*. We have seen that when the separate atoms both have closed shells only, half the electrons are binding electrons and half the electrons loosening electrons, so that in agreement with experiment no binding is possible. It is only for atoms where all the electrons are not in closed shells that an excess of binding electrons over loosening electrons is possible as the nuclei approach. As Hund emphasized during the discussion on this paper, we may also regard each atom as contributing a definite number of resultant binding electrons (binding electrons less loosening electrons) to the bond. This number at once gives the valency of the atom. It is in general identical with the number of non-paired electrons; hence the essential agreement with the results of the Heitler-London theory. The discrepancies, however, point to the former definition of valency being the more advantageous. It must be emphasized, all the same, that the above equating of the number of resultant binding electrons to the valency is not always applicable in the sense that it gives the number of atoms that actually become attached, but that in individual cases further investigation must be made as to how many electrons in a particular bond would act as binding electrons and how many as loosening electrons, before we can predict theoretically whether that binding is possible.* The discrepancies between the results of the above method and those of the Heitler-London valency theory (cf. O_2 and CH above) are, as we mentioned above, chiefly due to our taking account of the P-states (degeneracy) and the resulting fact that a π-shell (like a δ-shell, &c.) is not closed until it contains 4 electrons. In spite of its double bond, O_2 can therefore have a $^3\Sigma$-state as fundamental state. If the molecule contained only shells of two electrons, we should obtain the same results as Heitler and London.

Another important point is that by this method the instability of terms of higher manifoldness (such as the quintet and septet states of N_2) is obtained in the same way as in Heitler and London's theory, i.e. it is due to the fact that a large number of electrons must occupy the higher shells.

The interpretation of the spectrum of N_2[1] still involves difficulties, as has been discussed by Hund † in detail. It looks as if,

* Cf. especially the footnote on p. 173.

† F. Hund, *Zeitschr. f. Physik*, 63, 719 (1930).

in this case as in most others, a great deal more experimental material will have to be collected. Except in the cases of H_2 and He_2, in fact, no spectrum or term scheme of any diatomic molecule is known really completely.

D. Some Remarks on Polyatomic Molecules *

Classification of Electronic Terms.—All we have said hitherto refers, broadly speaking, to diatomic molecules only. The theory of molecules containing more than two atoms is still in its infancy, particularly the theory of the electronic states. For linear molecules (CO_2, C_2H_2, HCN, &c.) the classification of the electron terms will be completely analogous to that of diatomic molecules. This will still apply to a certain extent to molecules which are approximately linear, except that the degeneracy of the Π-terms, Δ-terms, &c., is removed and we have to distinguish between Π^+-terms and Π^--terms, &c.† For non-linear molecules the above classification is no longer possible. The resultant spin vector S, however, retains its meaning so long as the multiplet splitting is slight.

The Term Scheme.—For the determination of the term multiplicity there are available exactly the same three methods as in the case of the diatomic molecule (see above), although none of them has been carried out strictly for molecules containing more than two atoms. A complication arises here from the fact that the polyatomic molecule can be split up into atoms in a great variety of ways. The individual atoms may be detached successively, i.e. we may investigate the dissociation into radical + atom; or the molecule may be separated into two radicals, or the internuclear distances of all the atoms may be increased simultaneously. From this it follows, conversely, that the term manifoldness obtained when two definite atoms or groups of atoms are brought together must agree with that obtained from two other atoms or groups of atoms which form the same molecule. When the internuclear distance is large, of course, it is not obvious without further investigation which terms belong together and form one and the same electron term in the complete molecule.

The relationship with the united atom must be extended in

* Mulliken (*Chem. Rev.*, 9, 347 (1931)) has recently come to very similar conclusions.

† Cf. Hund, *Zeitschr. Astrophys.*, 2, 217 (1931); *Erg. exakt. Naturwiss.*, 8, 147 (1929).

polyatomic molecules by the relationship to the united groups of atoms or to a united molecule. For example, C_2H_2 will be compared with N_2,* H_2CO with O_2, &c.

The method for determining the term manifoldness from the electronic configuration will in linear polyatomic molecules again be similar to that for diatomic molecules, and to this is due the similarity between N_2 and C_2H_2 and HCN in many respects (Mecke, Brüche). As the author has shown,† even the excited electronic states of C_2H_2 seem to correspond to those of N_2; similarly for H_2CO and O_2. These facts strongly support the applicability and advantage of this method even for polyatomic molecules.

Problems of Valency and Binding.—With diatomic molecules we were only interested in the problem whether a molecular state is stable or unstable, or whether a molecule is stable in itself, i.e. whether the lowest molecular state is a stable molecular state and lies lower as regards energy than the state of two separate normal atoms. We shall refer to this as the *physical stability* of a molecule. (Mulliken ‡ calls it *molecular stability*.) In this sense molecules like CH, BH, CN, &c., as well as CH_2, NH_2, &c., are stable.§ The chemist, however, does not regard such molecules as stable. For *chemical stability* a further condition is required over and above those necessary for physical stability, namely, it is necessary that the molecule should be stable on colliding with or repelling similar molecules, for only then can the molecule be produced by chemical means, i.e. be chemically stable. In this sense the radicals named above are unstable.|| According to the ordinary chemical idea of valency, molecules in which all the valencies are saturated are chemically stable and conversely, in chemically stable molecules all the valencies are saturated. Experimentally, however, this converse does not hold in general (as is shown particularly clearly by the chemical stability of the molecules NO and NO_2), although it is true in many cases.

It would be of great importance if we could theoretically infer

* R. Mecke, *Zeitschr. f. Physik*, **64**, 151 (1930).

† G. Herzberg, *Trans. Farad. Soc.*, **27**, 378 (1931).

‡ R. S. Mulliken, *Phys. Rev.*, **32**, 186, 761 (1928).

§ He_2 is physically unstable.

|| Molecules which readily react chemically with others are nevertheless to be regarded as chemically stable molecules in the above sense; e.g. NO is to be regarded as chemically stable although it immediately reacts with O_2. In any case it can be produced chemically and in itself is very stable.

the chemical stability or instability of a polyatomic molecule from the known properties of the atoms or groups of atoms of which it is built up. This means as a rule that we have to investigate whether two groups of atoms repel or attract one another as they approach. Then, of course, we should essentially obtain a theoretical basis for the chemist's conception of valency, for the latter is in general valid.

Heitler and London have put forward the theory that the formation of an electron-pair from electrons which were previously unpaired is essential for the saturation of a valency, and that all those molecules in which all the electrons are paired are chemically stable or saturated. This, then, is the case when the fundamental state is a singlet state ($S = 0$). This conception agrees in the main with the chemical valency theory (stability of molecules such as CO, CO_2, CH_4, OH_2, &c.), but suffers from the same imperfections and involves some other difficulties.

To begin with the Heitler-London theory is contradicted by the *chemical stability* of the molecules O_2, NO, and NO_2. As its fundamental state O_2 (see above) has a $^3\Sigma$-state, i.e. two free spins not joined in a pair. According to Heitler and London, therefore, two O_2 molecules should attract one another. The same is true of NO, which has a $^2\Pi$-state as fundamental state, and NO_2, whose fundamental state is in any case a doublet state. In the latter the free valency might possibly be regarded as the reason for the considerable polymerization which occurs at low temperatures. In NO and O_2, however, polymerization of this kind has not been observed; two molecules of NO or O_2 accordingly do not attract one another, in spite of their unsaturated spins.

Further, the *chemical instability* of compounds such as BH, BH_3, P_2 cannot be explained by means of the Heitler-London theory. All these compounds have a singlet state as fundamental state, all the valencies are saturated in the Heitler-London sense, so that the molecules should be chemically stable. This would apply all the more to BH_3, seeing that the maximum number of valencies is saturated. Nevertheless these molecules, as is well known, are chemically unstable.

The examples mentioned (apart from O_2) cannot be satisfactorily explained by the ordinary valency idea either, nor by the Lewis theory of electron pairs.

It is natural to assume that a further development of the method of electronic configuration, which has turned out fairly satisfactory for diatomic molecules, will lead to simple results in the case of

polyatomic molecules also, and in particular will also be capable of explaining the above-mentioned exceptions without the necessity for extensive and involved calculations. Meanwhile this extension to polyatomic molecules is hindered by the fact that as yet there is no theory of the motion of electrons in a system of many centres of force, i.e. nothing can be said about the quantum numbers of the electrons in a polyatomic molecule. As we shall show below, it is only in the case of a few linear and pseudo-diatomic molecules that this is possible.

We accordingly make the same assumptions as were found to be justified in the diatomic molecule, namely that every atom has a definite number of resultant binding electrons (Hund), this number being in general equal to the valency, and further that closed shells always give as many binding electrons as loosening electrons. This rule, as we saw, usually gives agreement with experiment, but must, especially in cases which do not agree with the valency theory, be extended by more accurate investigation as to whether the binding in question has an excess of binding electrons.* We assume that in polyatomic molecules also the strength of binding is determined by the *excess* of binding electrons. Here we also make use of the experimental fact (see further below) that definite electrons can apparently be ascribed to each bond.

This at once leads in the first place to the repulsion between two molecules of H_2, N_2, F_2, &c., for these have closed shells only, which, by hypothesis, give equal numbers of binding electrons and of loosening electrons. The saturation mechanism acts just as in the Heitler-London theory. The present method, however, appears to give in addition the repulsion (required by experiment) between two O_2 molecules or two NO molecules, while O_2 and O, say, or NO and O, do not repel one another. In the case of O_2 there are two π-electrons in addition to closed shells. These, however, are loosening electrons, and it is probable that they have the same loosening effect on the two oxygen atoms which collide as two O_2 molecules approach one another. An attraction, which on the basis of Heitler and London's theory would necessarily occur, would therefore be impossible. Exactly the same is true of NO, which in addition to closed shells has *one* loosening electron. On

* Just as in the case of diatomic molecules the rule that a bond can only exist if the number of binding electrons exceeds the number of loosening electrons is of course not quite exact, as there are quantitative differences between the binding and loosening effects of the different shells.

the other hand, the effect is quite different when an oxygen atom is brought near O_2 or NO, for the oxygen atom brings two binding electrons with it, so that a binding can take place with O_2 as with NO.*

A more detailed explanation on a firmer basis is possible in the case of hydrides, where as a first approximation the hydrogen nucleus may be thought of as united with the atoms in question and the polyatomic molecule then treated as diatomic. Thus e.g. BH resembles the carbon atom. Hence two BH groups will no more repel one another than two carbon atoms will, although their fundamental state is $^1\Sigma$, because according to the above scheme more electrons act as binding electrons than as loosening electrons. Chemically B_2H_2 is unstable, presumably for the reason for which C_2 is chemically unstable. Here, however, we shall not discuss the various steps of advance to the stable product B_2H_6, but shall merely touch on the question why B_2H_6 is stable and BH_3 not, although the maximum number of valencies is really saturated in BH_3. The electronic configuration of BH_3 resembles that of the oxygen atom. In the above scheme, therefore, two BH_3 groups give the configuration $\sigma_g^2\sigma_u^2\sigma_g^2\sigma_u^2\pi_u^4\sigma_g^2\pi_g^2$, which gives two pairs of resultant binding electrons, as in O_2.† In agreement with experiment we accordingly come to the conclusion that two BH_3 groups attract one another fairly strongly. According to the above the binding would be regarded as double. It is safer, however, not to draw two dashes between the BH_3 groups, as this might give rise to the idea that boron is pentavalent, whereas according to the above rule boron is still to be regarded as trivalent, because it can have only three binding electrons. That the compound B_2H_6 is nevertheless formed is due to the fact that in BH_3, as in the oxygen atom, not all the shells are complete. The two dashes which we might think of drawing between the two BH_3 groups belong to these as a whole and not to the boron atoms. The BH_3 groups probably have a triplet state as fundamental state,‡ like the oxygen

* We may well assume that the two loosening electrons of O_2 are distributed over the two atoms in such a way that as the third oxygen atom approaches only one is effective and a resultant binding electron is left for the binding in question, so that attraction, though perhaps a feeble one, is possible, in agreement with experience (O_3).

† Like C_2H_4, which also resembles O_2, B_2H_6 should exhibit *cis-trans* isomerism in its derivatives, as obviously the same line of argument applies as has been used for ethylene by Hückel (*Zeitschr. f. Physik*, 60, 423 (1930)).

‡ This assumption that BH_3 has a triplet state as fundamental state, however, is not necessary for the explanation of the mutual attraction of two BH_3 groups.

atom. This would again be a case (similar to that of the $^4\Sigma$-term of CH) where a hydrogen atom is firmly bound to another atom although their spins are parallel. This is again due to π-degeneracy.

We have already indicated above that C_2H_2 very probably has the same electronic configuration as N_2, namely $\sigma_g{}^2\sigma_u{}^2\sigma_g{}^2\sigma_u{}^2\pi_u{}^4\sigma_g{}^2$. In the separation into CH + CH this obviously gives the configuration $\sigma^2\sigma^2\sigma\pi^2$ of the separate CH groups. The lowest state of this configuration, however, is very probably $^4\Sigma$, a state which, as we have said, may very well lie below the lowest state ($^2\Pi$) of CH hitherto known. At any rate the binding of the two CH groups in C_2H_2 is triple, as in agreement with the ordinary ideas there are three pairs of resultant binding electrons. It is not, as might be thought, necessary for the formation of the fundamental state of C_2H_2 that the carbon atom should previously be excited into the ^5S-state, as the $^4\Sigma$-state of CH can also arise from normal carbon.*

Considerations similar to those for C_2H_2 apply to HCN.

Finally, we shall discuss P_4 quite briefly. As was shown above, N_2 resembles the inert gases. It has a large binding strength and a large excitation potential, and all its shells are complete. Two normal N_2 molecules repel one another just as two atoms of an inert gas repel one another. As in the case of helium, however, we may expect a normal N_2 molecule and an excited N_2 molecule to be capable of attracting one another owing to the diminution in the number of loosening electrons. The behaviour of P_2 should resemble that of N_2, except that the energy relationships will be different owing to the change in the principal quantum number (see above). It is at least conceivable that as a result the state arising from one normal molecule and one excited molecule will, in contradistinction to that of N_2, lie lower than the state of two separate normal molecules. The chemical instability of P_2 would thus be explained. This brings out very clearly that *chemical stability or instability is often a merely quantitative matter* and that it is not in general possible to give qualitative rules.

Electron Transitions in Polyatomic Molecules.—If it is correct to assume, as we did above, that the separate electrons of a polyatomic molecule distribute themselves, so far as they can be distinguished at all,† among the different bonds (dashes), it must be possible to

* The same is perhaps true for C_2H_4 and C_2H_6 also (cf. Hund, *Erg. exakt. Naturwiss.*, 8, 147 (1929)).

† We take it that it will be impossible to distinguish experimentally between say the electrons of the various C—H bonds, e.g. in a CH_3 group.

excite single bonds in such a way that practically only the strength of one bond is affected by the electron jump. This state of affairs, in fact, seems to be actually observed in certain cases. In the methyl halides G. Scheibe and the author * found that one vibration frequency in the excited state is the same for all the halides, i.e. it must be a frequency characteristic of the CH_3 group, not noticeably affected by the excitation of the carbon halogen bond which is apparently concerned in the observed transition. In the fundamental state the corresponding frequency is only 100 cm.$^{-1}$ greater. As the author has shown,† analogous considerations appear to hold for H_2CO and C_2H_2. That the electronic excitation in the methyl halides lies in the carbon halogen bond is also proved by the fact that the intensity decreases very rapidly in the series of bands obtained, as may be expected from suitable adaptation of the Franck-Condon principle to polyatomic molecules, if the potential curves of the CH_3 group are not essentially affected by the excitation. In H_2CO, where the one chiefly occurring vibration frequency of the excited state probably corresponds to the CO vibration, the phenomena are quite different. The intensity of the bands first increases and then decreases, as the potential curve for this vibration is much altered.‡

In this connexion another fact is very suggestive, namely that in CH_3I only two of the ultra red or Raman frequencies (524 and 1250 cm.$^{-1}$) make themselves evident in the ultra-violet as feeble bands at the long wave length side of the ordinary bands, while a third lying between them (800 cm.$^{-1}$) certainly does not appear at all. The ultra red structure of the corresponding band, however, shows that the vibration is at right angles to the axis of the molecule (C—I). Such a vibration will not be affected at all by the excitation of the C—I bond and hence, according to Franck and Condon, only those transitions occur for which the vibrational quantum number of this vibration is not altered at all.

Considerations like those just adduced should play an important part in the interpretation of the ultra-violet absorption spectra of polyatomic molecules. As should be obvious from what has been said above, they also have an important bearing on the explanation of the mechanism of valency.

* G. Herzberg and G. Scheibe, *Zeitschr. f. phys. Chemie*, B, **7**, 390 (1930).

† G. Herzberg, *Trans. Farad. Soc.*, **27**, 378 (1931).

‡ A second vibration frequency apparently associated with the CH_3 group is manifested by bands which, in agreement with what we have said above, adjoin the principal bands with rapidly diminishing intensity.

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